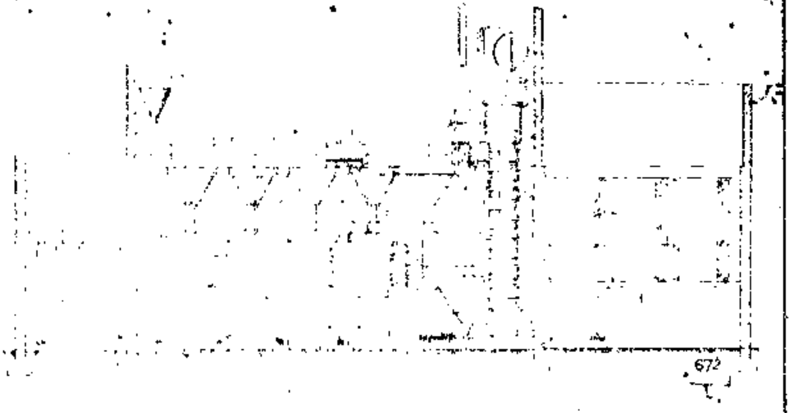
SCOTT PATENT

OIL EXTRACTION PLANT



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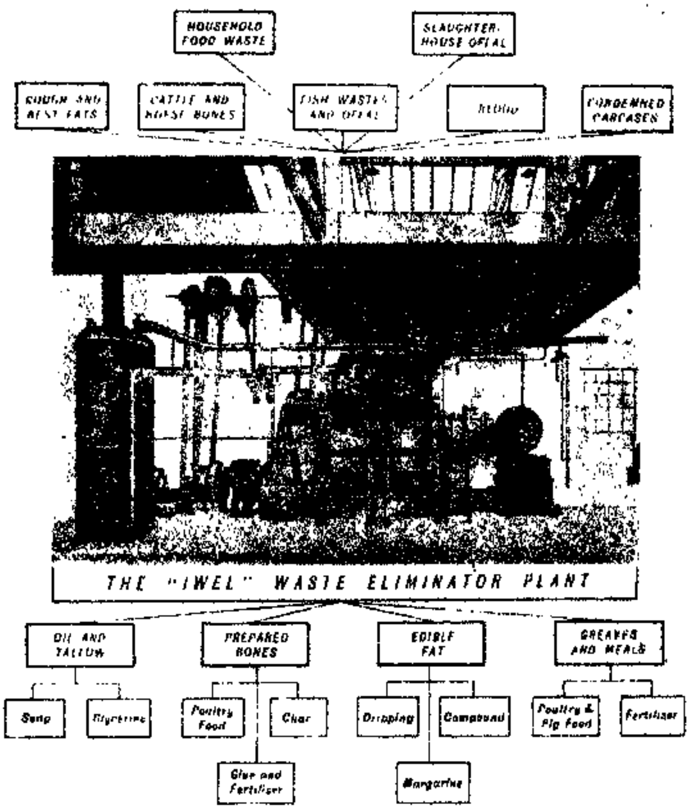

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MANUALS OF CHEMICAL TECHNOLOGY—IX

ANIMAL AND VEGETABLE OILS, FATS, & WAXES

Their Manufacture, Refining, and Analysis, including
the Manufacture of Candles, Margarine, and Butter

A PRACTICAL TREATISE

By

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1920

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CHAPTER I

Nature of Animal and Vegetable Oils and Fats

CHAPTER I

NATURE OF ANIMAL AND VEGETABLE OILS AND FATS

LITERATURE

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INTRODUCTION

Fats and fatty oils occur disseminated throughout the tissues of almost all animals and seeds in the form of minute globules enclosed within a thin skin, forming a reserve food for the organism. Pressure alone will not usually suffice to break up the animal fat cells; the tissue must be heated when it shrivels up as it loses water, while the increasing temperature causes the fat globules to expand, burst the cell, and flow out as a liquid mass. In the case of vegetable seeds pressure alone often secures the expulsion of the oil, although here, too, the operation is much facilitated by a gentle heat.

The difference between a fatty oil and a fat is merely one of physical condition due to temperature; an oil freezes into a fat, and a fat melts to an oil. In a warm climate a substance will always appear as an "oil," whereas the same body will appear to the inhabitants of a colder clime as a solid fat. Thus, for example, coco-nut oil is liquid in India but solid in England, where it is used by vegetarians in place of butter. As previously explained, "mineral" oils are quite different in chemical character to a vegetable or animal oil.

Chemically considered, fats and fatty oils are bodies produced by the chemical union of glycerol with fatty acids. *Glycerol* is a trihydric alcohol, of formula $C_3H_5(OH)_3$. It is capable of combining with three molecules of fatty acids to form "triglycerides," thus:—

$$C_3H_5\begin{array}{l}.OH\\.OH\\.OH\end{array} + 3.R.OH = C_3H_5\begin{array}{l}.OR\\.OR\\.OR\end{array} + 3H_2O$$

Glycerol. Fatty acid. Triglyceride of fatty acid. Water.

Where R stands for the radical of the fatty acid.

Fats and fatty oils are merely mixtures of these triglycerides of the fatty acids. The three glycerides which usually predominate in most fats are solid tristearin, solid tripalmitin, and liquid triolein—the respective glycerides of stearic, palmitic, and oleic acids. Solid fats usually contain much stearin and palmitin, but little olein; liquid fats, on the other hand, consist principally of olein. Other fats and oils exist (*e.g.*, linseed and castor oils) which are composed of glycerides of other acids than those mentioned above. We append a list of the principal fatty acids occurring in natural fats and oils, together with the names and formulæ of their triglycerides.

FATTY ACIDS AND THEIR TRIGLYCERIDES.

Saturated Acids of the Acetic Series. $C_nH_{2n+1}.COOH$.

Acid.	Formula.	M.P. (°C.)	B.P. (°C.)		Corresponding Glyceride.	Formula.
Formic -	$H.COOH$	8.3	101		Formin -	$C_3H_5(O.HCO)_3$
Acetic -	$CH_3.COOH$	16.5	118		Acetin -	$C_3H_5(O.CH_3CO)_3$
Propionic -	$C_2H_5.COOH$	-22.0	141		Propionin -	$C_3H_5(O.C_2H_5CO)_3$
Butyric (normal iso)	$C_3H_7.COOH$	-7.9 79.0	162 154		Butyrin -	$C_3H_5(O.C_3H_7CO)_3$
Valeric (normal iso)	$C_4H_9.COOH$	58.5 51.0	185 174		Valerin -	$C_3H_5(O.C_4H_9CO)_3$
Caproic -	$C_5H_{11}.COOH$	-8.0	205		Caproin -	$C_3H_5(O.C_5H_{11}CO)_3$
Aethanthylic -	$C_6H_{13}.COOH$	10.0	223		Aethanthylin -	$C_3H_5(O.C_6H_{13}CO)_3$
Caprylic -	$C_7H_{15}.COOH$	16.5	237.5		*Caprylin* -	$C_3H_5(O.C_7H_{15}CO)_3$
Pelargonic -	$C_8H_{17}.COOH$	12.5	186	At 100 mm. pressure.	Pelargonin -	$C_3H_5(O.C_8H_{17}CO)_3$
Capric -	$C_9H_{19}.COOH$	31.3	200		Caprin -	$C_3H_5(O.C_9H_{19}CO)_3$
Undecylic -	$C_{10}H_{21}.COOH$	28.0	212		Undecylin -	$C_3H_5(O.C_{10}H_{21}CO)_3$
Lauric -	$C_{11}H_{23}.COOH$	43.6	225		Laurin -	$C_3H_5(O.C_{11}H_{23}CO)_3$
Tridecylic	$C_{12}H_{25}.COOH$	40.5	236		Tridecylin -	$C_3H_5(O.C_{12}H_{25}CO)_3$
Myristic -	$C_{13}H_{27}.COOH$	53.8	248		Myristin -	$C_3H_5(O.C_{13}H_{27}CO)_3$
Pentadecatoic	$C_{14}H_{29}.COOH$	51.0	257		Pentadecatoin	$C_3H_5(O.C_{14}H_{29}CO)_3$
Palmitic -	$C_{15}H_{31}.COOH$	62.0	268		Palmitin -	$C_3H_5(O.C_{15}H_{31}CO)_3$
Margaric -	$C_{16}H_{33}.COOH$	60.0	277		Daturin -	$C_3H_5(O.C_{16}H_{33}CO)_3$
Stearic -	$C_{17}H_{35}.COOH$	69.3	287		Stearin -	$C_3H_5(O.C_{17}H_{35}CO)_3$
Nondecylic -	$C_{18}H_{37}.COOH$	66.5	298		Nondecylin -	$C_3H_5(O.C_{18}H_{37}CO)_3$
Arachidic -	$C_{19}H_{39}.COOH$	77.0	...		Arachidin -	$C_3H_5(O.C_{19}H_{39}CO)_3$
Medullic -	$C_{20}H_{41}.COOH$	.	...		Medullin -	$C_3H_5(O.C_{20}H_{41}CO)_3$
Behenic -	$C_{21}H_{43}.COOH$	83.0	306 (60 mm.)		Behenin -	$C_3H_5(O.C_{21}H_{43}CO)_3$
Carnaubic -	$C_{23}H_{47}.COOH$	72.5	...		...	... ...
Hyaenic -	$C_{24}H_{49}.COOH$	77.5	.		..	... ...
Cerotic -	$C_{25}H_{51}.COOH$	78.0	...		...	... ...
Melissic -	$C_{29}H_{59}.COOH$	91.0	..		...	... ...

Unsaturated Fatty Acids of the Oleic Series. $C_nH_{2n-1}COOH$.

Acid.	Formula.	M.P. (°C.)	B.P. (°C.)	Corresponding Glyceride.	Formula.
Acrylic	$C_2H_3.COOH$	+13	140	...	... ...
Crotonic	$C_3H_5.COOH$	71.5	180.5	...	... ...
Iso-crotonic	$C_3H_5.COOH$	15.5	169	...	... ...
Angelic	$C_4H_7.COOH$	45	185	...	... ...
Tiglic	$C_4H_7.COOH$	65	198	...	... ...
Hypogaeic	$C_{15}H_{29}.COOH$		...	..	$C_3H_5(O.C_{15}H_{29}CO)_3$
Oleic	$C_{17}H_{33}.COOH$	14	223 (10 mm.) 250 (superheated steam)	Olein	$C_3H_5(O.C_{17}H_{33}CO)_3$

Unsaturated Fatty Acids of the Linolic Series. $C_nH_{2n-3}COOH$.

Acid.	Formula.	M.P. (°C.)	B.P. (°C.)	Corresponding Glyceride.	Formula.
Elaeostearic (Elaeomargaric)	$C_{16}H_{29}.COOH$	43	..	Elaeostearin	$C_3H_5(O.C_{16}H_{29}CO)_3$
Linolic	$C_{17}H_{31}.COOH$	below 18	...	Linolein	$C_3H_5(O.C_{17}H_{31}.CO)_3$

Unsaturated Fatty Acids of the Linolenic Series. $C_nH_{2n-5}COOH$.

Acid.	Formula.	M.P. (°C.)	B.P. (°C.)	Corresponding Glyceride.	Formula.
Linolenic	$C_{17}H_{29}.COOH$	Liquid	...	Linolenein	$C_3H_5(O.C_{17}H_{29}.CO)_3$

Unsaturated Fatty Acids of the Recinoleic Series.

Acid.	Formula.	M.P. (°C.)	B.P. (°C.)	Corresponding Glyceride.	Formula.
Recinoleic	$C_{17}H_{32}(OH).COOH$	4		Recinolein	$C_3H_5(O.C_{17}H_{32}(OH).CO)_3$

It may be noticed that monoglycerides and diglycerides, corresponding to the formulæ $C_3H_5\begin{array}{l}.OR\\.OH\\.OH\end{array}$ and $C_3H_5\begin{array}{l}.OR\\.OR\\.OH\end{array}$, exist in rancid or partially hydrolysed fats, while mixed glycerides of the formula $C_3H_5\begin{array}{l}.OR_1\\.OR_2\\.OR_3\end{array}$ (R_1, R_2, R_3, corresponding to three different acid radicals) certainly occur in small quantities in certain normal fats, *e.g.*, in ordinary butter-fat, also in tallow.

Fats are usually neutral bodies, but old or rancid fats often contain large quantities of free fatty acids, which may be extracted by sodium carbonate solution or by alcohol. Old palm oil, and some fish oils, often contain no less than 60 per cent. of free fatty acids.

While at ordinary temperatures some fats are white crystalline solids, others are fluids, fatty to the touch; all produce permanent grease-spots on paper; they are insoluble in water, slightly soluble in alcohol, easily soluble in ether, benzine, chloroform, carbon disulphate, and carbon tetrachloride. When distilled alone they decompose, producing vapours of acrolein; with high tension steam they distil with partial saponification into free acids and glycerol.

Pure fats are tasteless, odourless, and keep for years. When, however, they contain small quantities of nitrogenous animal or vegetable impurities they often turn rancid in the presence of air decomposing into free acids and glycerol by a process of enzyme hydrolysis. Oxygen is absorbed during this change, and the acids formed are often oxidised to oxyacids, while the glycerol is also partially destroyed. In air-tight vessels, in the absence of oxygen, fats do not become rancid.

When heated with an aqueous (but best with an alcoholic) solution of sodium or potassium hydroxide, fats are completely "saponified" into glycerol and the alkali salt of the fatty acid, thus:—

$$\underset{\text{Tristearin.}}{C_3H_5(O.C_{17}H_{35}CO)_3} + \underset{\text{Caustic soda.}}{3NaOH} = \underset{\text{Glycerol.}}{C_3H_5(OH)_3} + \underset{\substack{\text{Sodium stearate}\\ \text{(ordinary soap).}}}{3C_{17}H_{35}.COONa.}$$

The metallic or inorganic salts of the fatty acids are called "soaps."

Other bases, such as slaked lime, magnesia, and lead oxides, readily saponify most fats, the resultant soaps, however, being usually insoluble.

It should be particularly noticed that the alkali carbonates, such as sodium or potassium carbonates, will not saponify fats even when boiled with them at ordinary pressures. Heated under high pressure in autoclaves they readily saponify.

STATISTICS RELATING TO ANIMAL AND VEGETABLE OILS AND FATS IMPORTED INTO THE UNITED KINGDOM.

Articles.		Quantities.		Value.	
		1913.	1916.	1913.	1916.
				£	£
Oil, fish: viz., train, blubber, sperm, or head matter	*Tuns*	70,886	108,867	1,508,416	3,493,474
,, animal	*Cwts.*	224,324	51,776	298,026	120,270
,, coco-nut: unrefined	,,	622,801	422,435	1,342,469	1,087,313
,, ,, refined	,,	546,742	154,943	1,316,246	464,723
,, mineral jelly (including vaseline)	,,	19,626	41,865	45,322	87,390
,, olive: unrefined	*Tuns*	2,882	5,374	130,191	272,272
,, ,, refined	,,	6,163	5,180	385,257	344,307
,, palm (not including palm-kernel oil), unrefined	*Cwts.*	1,562,203	1,243,556	2,326,842	2,198,984
,, palm-kernel, unrefined	,,				
,, palm and palm-kernel, refined	,,	58,230	...	141,967	...
,, petroleum—					
Crude	*Gallons*	1,108,900	1,855	14,746	53
Lamp oils	,,	157,141,241	127,339,777	2,679,518	3,071,394
Motor spirit	,,	*100,858,017*	*161,410,824*	*3,803,397*	*9,974,293*
Spirit, other than motor spirit	,,	270	...	46	...
Lubricating oils	,,	67,962,493	83,167,754	2,472,514	5,295,113
Gas oil	,,	65,949,677	57,074,508	735,388	1,064,824
Fuel oil	,,	95,062,187	22,556,004	1,149,816	373,126
Other sorts	,,	24,178	5,430	1,381	277
,, seed—					
Castor	*Tons*	1,399	5,701	41,875	249,125
Cotton seed oil: unrefined	,,	1,070	712	31,748	28,574
,, ,, refined	,,	16,586	10,098	558,277	516,227
Linseed oil—					
Pure	,,	11,866	6	310,157	160
Not pure	,,	22	3	513	75
Rape-seed oil	,,	7,599	7,989	222,556	307,233
Other seed oils	,,	20,380	48,471	767,810	1,884,805
,, turpentine	*Cwts.*	560,330	430,780	768,800	903,384
,, essential—					
Natural	*Lbs.*	2,323,348	2,549,339	555,376	633,789
Artificial	,,	260,638	221,243	35,613	48,485
,, unenumerated	*Value*	...	...	129,407	195,794
Total of oil		...	...	21,773,674	32,615,464
Oil-seed cake, containing no dutiable ingredient—					
Cotton-seed cake	*Tons*	236,723	191,995	1,407,023	2,017,790
Linseed cake	,,	83,679	74,418	626,118	937,312
Rape-seed cake	,,	28,882	734	156,592	7,141
Unenumerated	,,	57,416	16,850	350,159	153,704
Total of oil-seed cake		406,700	283,997	2,539,892	3,115,947
Oleo-margarine or oleo oil, and refined tallow	*Cwts.*	377,557	650,584	858,130	2,086,489

Superheated steam or hot acids "hydrolise" fats into glycerol and free fatty acids, thus:—

$$\underset{\text{Tristearin.}}{C_3H_5(OC_{17}H_{35}CO)_3} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Glycerol}}{C_3H_5(OH)_3} + \underset{\text{Stearic acid.}}{3C_{17}H_{35}COOH}$$

Certain ferments present in seeds (especially in castor seeds) readily split fats into glycerol and fatty acids at ordinary temperatures. See under **Candles.**

The fats and fatty oils are used for making soap, candles, lubricants, varnishes, paints, for burning in lamps, and for edible purposes. The industry is an enormous one.

Fats have been artificially synthesised; for recent work see Grün and collaborators, *Ber.*, 1907, xl., 1778-1791, 1792-1801, and later papers.

The following numbers refer to the *Exports* from the United Kingdom:—

		Quantities.		Values.	
		1913.	1916.	1913.	1916.
OILS, EXCEPT MEDICINAL:—					
Coco-nut: unrefined	*Cwts.*	62,067	13,529	£127,465	£29,539
refined	,,	58,913	39,293	141,777	125,140
Olive: unrefined	*Tons.*	20	5	1,183	444
refined	,,	304	209	45,487	33,932
Palm and palm-kernel: unrefined	*Cwts.*	20,995	60,799	43,096	136,458
refined	,,	15,168	30,232	24,169	58,224
Seed:—					
Castor *	*Tons.*	10,818	3,084	301,839	175,321
Cotton-seed oil: unrefined	,,	522	171	15,453	6,327
refined	,,	25,013	2,407	755,083	101,197
Linseed oil: pure	,,	26,738	23,351	794,150	971,806
not pure	,,	3,173	1,443	86,683	56,115
Rape-seed oil	,,	5,839	3,940	175,846	180,327
Soya bean oil	,,	9,390	4,554	294,238	182,415
Other seed oil	,,	2,287	1,620	61,240	70,476
Total of seed oils	,,	83,780	40,570	£2,484,532	£1,743,984
Essential	*Lbs.*	363,787	536,482	111,510	177,109
Unenumerated	*Value.*	...	...	1,483,286	1,671,994
Total of oils	,,	...	...	£4,462,505	£3,976,824
OIL-SEED CAKE, NOT SWEETENED:—					
Cotton-seed cake	*Tons.*	7,762	11	36,638	142
Linseed cake	,,	6,149	61	47,394	804
Rape-seed cake	,,	970	2	5,121	38
Soya bean cake	,,	29,903	3,830	208,899	36,132
Unenumerated	,,	8,664	1,648	56,292	13,149
Total of oil-seed cake, not sweetened	,,	53,448	5,552	£354,344	£50,265
OLEO-MARGARINE AND REFINED TALLOW AND ANIMAL FAT	*Cwts.*	258,508	74,659	£526,466	£223,076

* Included in "Other seed oil" prior to 1913.

CHAPTER II

Manufacture of Animal Oils and Fats

CHAPTER II

MANUFACTURE OF ANIMAL OILS AND FATS

Animal Oils and Fats are usually obtained by heating the tissues rich in oil or fat, so as to cause the bursting of the fat-containing cell.

Tallow (beef or mutton fat).—The "rough fat" fresh from the slaughter-house is placed in a lead-lined tank provided with a steam coil for heating, and an outlet passing to a chimney stack for the escape of offensive vapours. Hot water is poured on to the fat, and the vessel and its contents heated for some hours by the steam coil. On settling, the melted fat rises to the surface as a clear layer, and is drawn off through outlet taps into another vessel. The fat is now ready for use, unless when made from inferior materials, when it must be refined and bleached as described below.

The residue of fatty matter left in the tank is acidified with a little sulphuric acid, and steam again turned on. The small amount of sulphuric acid does not hydrolise the fats, but partially destroys the cell membranes, thus setting free their occluded fat, which is run off as before into another vessel. An inferior variety of fat is thus obtained.

Tallow for **soap-making** (but not for comestible purposes) is rendered in digesters under pressure. Fig. 1 shows one of the large modern rendering tanks used in the American packing industry; made of riveted steel plates and capable of standing a working pressure of four or five atmospheres, the largest ones are 8 ft. in diameter and 20 ft. high. They are provided with safety valves, and discharge through a gate valve at the bottom. The tank is filled to within a foot of the junction of the upper cone and the cylindrical portion of the vessel—the material (in Chicago) often consisting of putrid carcasses of animals which have died in transit, diseased flesh, and other waste products unfit for comestible products. Then live steam at 40-50 lbs. pressure is turned on, and the contents of the boiler heated for eight to ten hours or so, the internal temperature being maintained at 130°-140° C.

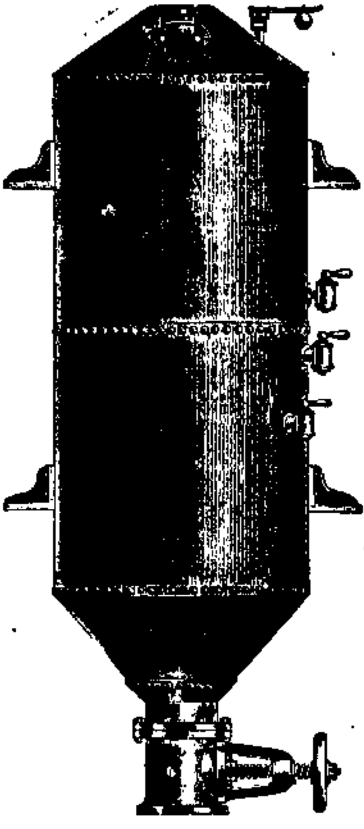

FIG. 1.—Packers' Rendering Tank.

Two air-cocks carry away the offensive fumes evolved during the heating. Finally the steam is turned off, the vent-pipes opened to allow the steam in the tanks to blow off, and the fat is allowed to settle. The clear liquid fat floating on the surface of the water in the tank is now drawn off through the top draw-off cock, and, as the level in the tank subsides, through the lower ones in succession. Finally, water is pumped in from below, so as to raise the level of the fat (which, of course, floats upon the water) so that it too may be withdrawn through the stop-cocks.

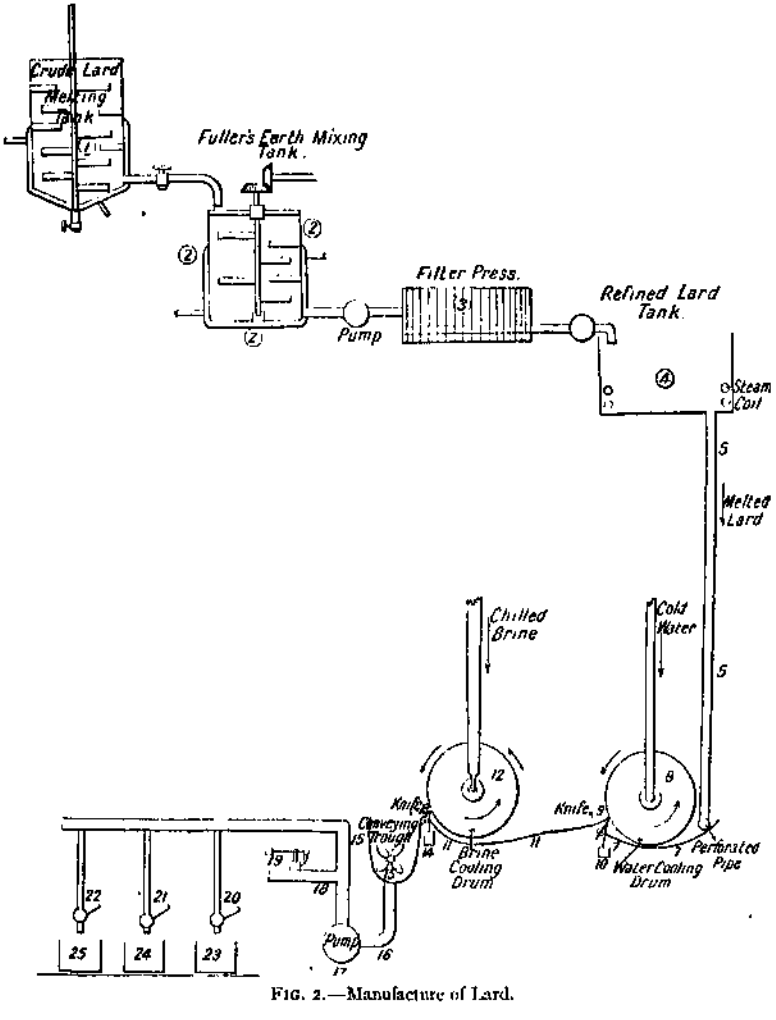

FIG. 2.—Manufacture of Lard.

Last of all the valve at the bottom of the tank is opened, and the contents run out into a series of settling tanks and catch basins to retain fat globules still in the water. A sludge settles at the bottom of these tanks; it is drawn off and pressed. The liquid running from the tanks flows into evaporators (vacuum, triple effect) where it is boiled down into a thick "soup." The sludge press-cakes are now mixed with this, and the mass sold as "Tankage Fertiliser."

Manufacture of Lard.—Lard is the fat of the hog, which is separated from the slaughtered animal and worked up as described above. It is refined by treating with fuller's earth, passing through a filter press, and cooling by running over rotating drums chilled internally by cold water or refrigerated brine.

Fig. 2 shows a typical lard-refining plant. The crude fat is melted in the iron tank (1), whence it is run out into the mixing pot (2), when 1-5 per cent. of fuller's earth is run in (the exact amount depending upon the quality of the fat treated), and the hot melted fat is agitated with this for a few minutes and is then run through a filter press (3) to free it from the fuller's earth. Then it is run into a collecting tank (4), whence it is run down a pipe (5), and enters a horizontal perforated pipe at the bottom, whence the hot lard, at about 140° F., pours out into a sheet-iron trough (7). Here it is caught up in the form of a film by a rotating cooling drum (8) (through the interior of which a stream of cold water circulates, the water entering through the axle of the drum). The fat film caught up on this is partially cooled, and passing over the drum is scraped off by a knife (9), which is kept pressed against the rotating drum by a weight (10). The partially cooled fat now runs into another iron tray (11), and is once more caught up and carried round as a film on the surface of another rotating drum (12) (this second drum being filled with chilled brine, which enters the drum through the centre axle). Here the final cooling is achieved, and the almost solid fat is carried round on the surface of the drum and scraped off by the knife (13), which is kept pressed tightly against the drum by the weight (14). The soft, partially solidified fat drops into the conveying trough (15), where it is broken up and moved along by the blades of a conveying shaft running along the centre of the trough. The fat is still fluid enough to pass down the pipe (16), whence it is pumped by the pump (17) up the pipe (18), and thence to the outlet pipes (20, 21, and 22). From these it is drawn off in weighed amounts into the reception vessels below (23, 24, and 25). (19) is a safety valve in case the pipes get blocked up with solidified lard.

Manufacture of Oleo Stearin and Oleo Oil from Beef Fat

The fat from the recently slaughtered animal is rapidly removed and plunged into a vat, and washed with warm water until free from blood and other impurities, hardened by immersion in ice water, chopped into a fine mass by a machine A (Fig. 3), and melted at 70°-75° C. in a steam-jacketed pan B, provided with slowly moving mechanical agitators. The mass is allowed to settle, salt being strewn over the surface of the liquid in order to accelerate the settling out of membranes and connective tissue (which collect at the bottom). Next the clear oil is siphoned over to another series of melting kettles, C, usually situated on a lower floor. More salt

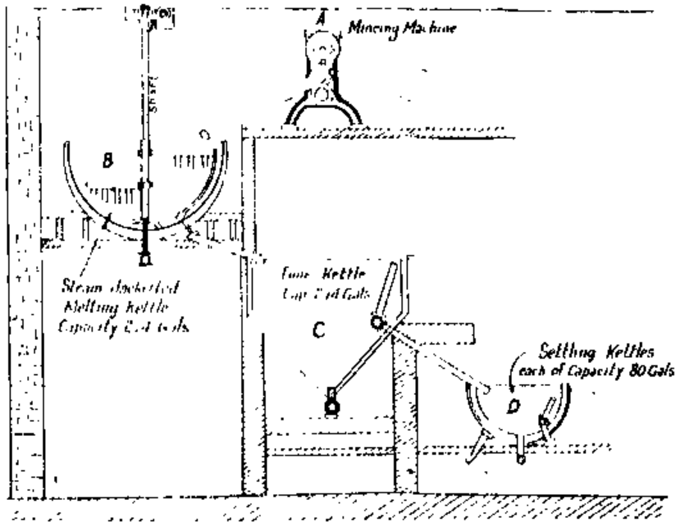

Fig. 3.—Manufacture of Oleo Stearin and Oleo Oil from Beef Fat.

is added, and the temperature maintained at 70°-80° C. until a second settling is complete. The fat, now free from membrane and connective tissue, is siphoned into shallow settling tanks and allowed to stand three to five days at a temperature (peculiar to each fat) which experience shows is best suited for allowing the stearin to crystallise. This stearin forms a crust over the surface, and the rest settles at the bottom, leaving a clear oil between. The crystallisation completed, the crust is broken into fine fragments by vigorous mechanical stirring, and the pasty mass thus obtained conveyed to a revolving table surrounded by skilled workmen, who wrap the mixture into small packages in canvas cloth (each containing about 3 lbs. weight), place them in hydraulic presses, and separate the oleo oil by great pressure slowly applied. The oil flows from the presses into large receiving tanks, while the solid stearin remains in the press as a cake, which is mixed with cotton-seed oil, and used for making lard substitute. The oleo oil is converted into margarine.

Caul fat yields about 50 per cent. oleo oil and 30 per cent. solid stearin, the precise yield varying considerably according to the temperature of pressing, the amount of tissue, and the quality of fat.

For success in this industry it is absolutely essential that the fat be obtained from the animal as soon after death as possible. In the United States the works are actually situated in the slaughter-houses, so that the animals are treated immediately after slaughtering. The industry originally developed in England, but owing to the neglect of this simple factor, and the consequent necessity of carting the flesh over long distances to the factories before treating, the quality of the product produced under such conditions could not compete with the American product, and consequently the centre of the industry shifted to the large slaughtering depots in the United States.

Lard Stearin and Lard Oil are obtained by treating hog fat (lard) as above described. The oil is used for illuminating purposes, and the stearin for the manufacture of lard compound and soap (see page 176).

Fat from Garbage.—In large cities a considerable quantity of fat for soap-making is made by heating sewage or garbage in upright steel tanks of 6 tons capacity with live steam at 30 lbs. pressure for six to eight hours. The mass is run into vats, allowed to settle, and the free water and grease floating on it are run off by drop-pipes into separating tanks. The sludge is filtered through cloth, and the cakes of solid matter compressed and sold as manure.

Fat from Offal and Carcasses.—For this purpose a combined steam and vacuum process is often employed, especially in small abattoirs.

The installation consists of a large digester for the condemned carcasses and large offal, and a smaller one for the smaller scraps. Large top doors permit of diseased carcasses being loaded in whole, thus avoiding contamination in handling. All fumes and gases are drawn off under vacuum, which not only assists in breaking down the fibres of the meat, etc., but permits the foul vapours to be efficiently condensed in water, thus rendering the process free from nuisance. The liquid due to the steaming in the digester, together with the fat, is blown into the closed separating tanks. In these tanks the soup is separated by decanting swivel pipes, and the fat purified by a steam and water wash.

The soup may be evaporated and thus converted into a useful size for use in paper and cotton mills. The residue in the digester is dried and sold for poultry food.

Another successful method of treatment is described on pages 16-20.

Recovery of Grease from Wool Washing, Flannel Mills, Etc.

(Yorkshire Grease, Wool Grease, Wakefield Grease, Lanolin, etc.)

Large amounts are recovered in Yorkshire, especially in the neighbourhood of Bradford, as follows: The liquid flowing away from the woollen mills contains much grease. Before spinning, the natural grease of wool is removed in the form of an emulsion by washing with sodium carbonate solution or soap. The fluid, which is usually of a dark, dirty appearance, is allowed to flow into large tanks. Next an acid solution (usually sulphuric acid, but more recently acid sodium sulphate, derived from the manufacture of nitric acid, and sold as "Nitre Cake," has been employed) is run in. When the liquid is acid the grease separates as a dirty sludge. The liquid is now allowed to run away through cloth filters, which retain the separated grease.

In large works the grease is recovered by pumping the fluid through filter presses. In small works, however, the liquid is simply run through cloth bags, which are then squeezed in presses to remove excess of water.

Since the process of wool washing gives rise to very large volumes of waste liquors containing much free and combined fat, complications ensue when these liquors are run off into sewers. In the case of Bradford, £12,000 per annum is expended for sulphuric acid with which to separate the fatty matter from the sewage (see *Journ. Chem. Ind.*, 1909, xxxviii. 14). The recovered fatty acids were sold under the name **Yorkshire grease** or **Wakefield grease** at £6 per ton, and 40 tons per week are recovered from the sewage. In large wool-washing works the suds are treated before running to waste, the grease being converted into lanolin, soap, and lubricating oil. In a works of moderate size 50 tons of grease were obtained monthly, and sold at £9 to £10 per ton.

The crude grease thus obtained is purified by various patented processes, and brought into the market under the name "**lanolin**" (see also p. 141). Yorkshire grease from wool and soap-suds is often purified in cast-iron stills, at first over an open fire (4 tons of grease requiring sixteen hours), and finally for twenty to twenty-four hours with superheated steam. The product is known as "**distilled grease**" (see also p. 141).

The liquids run to waste contain large amounts of potassium salts. So far it has not been profitable to recover them. In Australia and other sunny countries natural evaporation of the waste liquids might yield a commercial product.

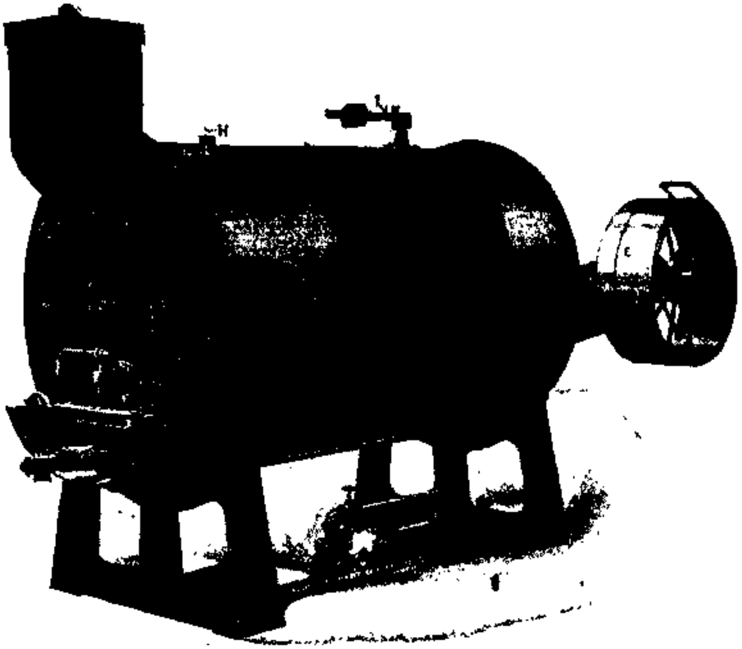

FIG. 4.—"Iwel" Rapid Fat Melter.
(Industrial Waste Eliminators, Ltd.)

Fat from Slaughter-house Bye-products, Food Scraps, Bones, Kitchen and Camp Waste.

Literature.—See H. E. FISH in "The World's Work," November 1918, p. 490.

Very successful plant is made for this purpose by the Industrial Waste Eliminators, Ltd., of London. The meat trimmings are first placed (by means of the charging hopper H) in the fat-melting boiler (Fig. 4), which is a steam-jacketed horizontal cylinder A, where by means of revolving beaters D the material is carried around the heated inner surface, and in this manner the moisture is evaporated and the fumes drawn away by means of a fan attached to the fume outlet C. The fat is thus rendered, and the liquid fat thus obtained is run off through the fat discharge cock J. A pressure of 80 lbs. is maintained in the steam jacket. The boiler will hold 15 cwt. of scraps. When all the melted fat possible is discharged through J, the door F is opened, and the solid residue is removed and placed in a turbine centrifugal fat extractor, shown in Fig. 5. This consists of a steam turbine A

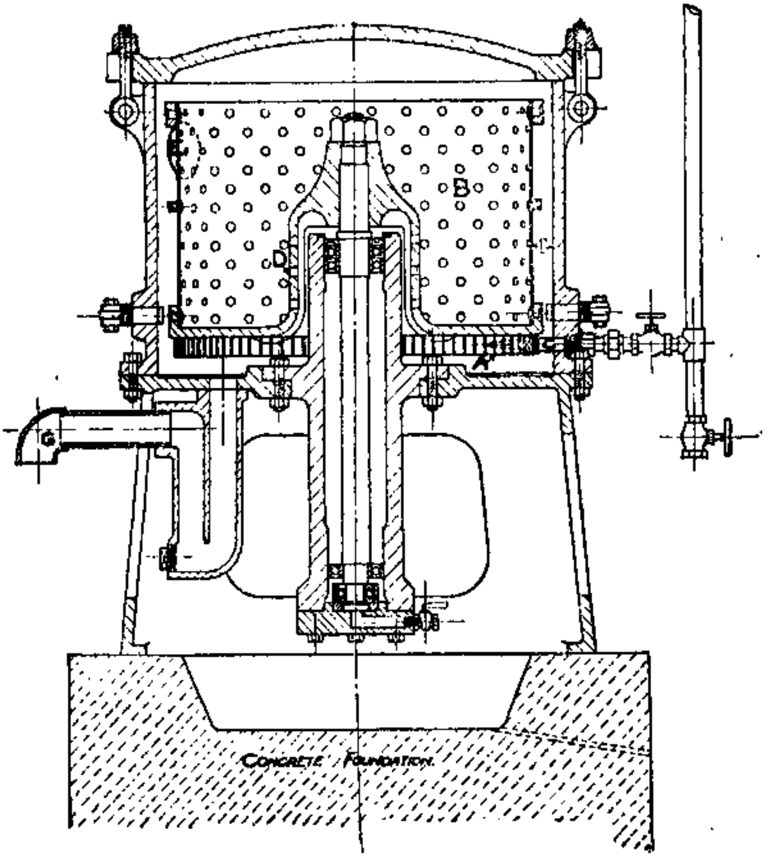

FIG. 5.—Turbine-Centrifugal Fat Extractor.
(Industrial Waste Eliminators, Ltd.)
Removable basket not shown in this figure.

directly connected with the steel perforated cage B, in which is dropped a removable perforated steel basket. This removable basket is fitted with a filter cloth lining. It is charged outside the machine with the material to be treated (two baskets being provided with each machine), and is then inserted in the cage B as shown in Fig. 6. The lid is next shut down and the steam turned on at C (Fig. 5). The turbine A is driven by a blast of steam from the nozzle C, impinging on blades attached to the bottom of the revolving steel cage B. The steam exhausts itself

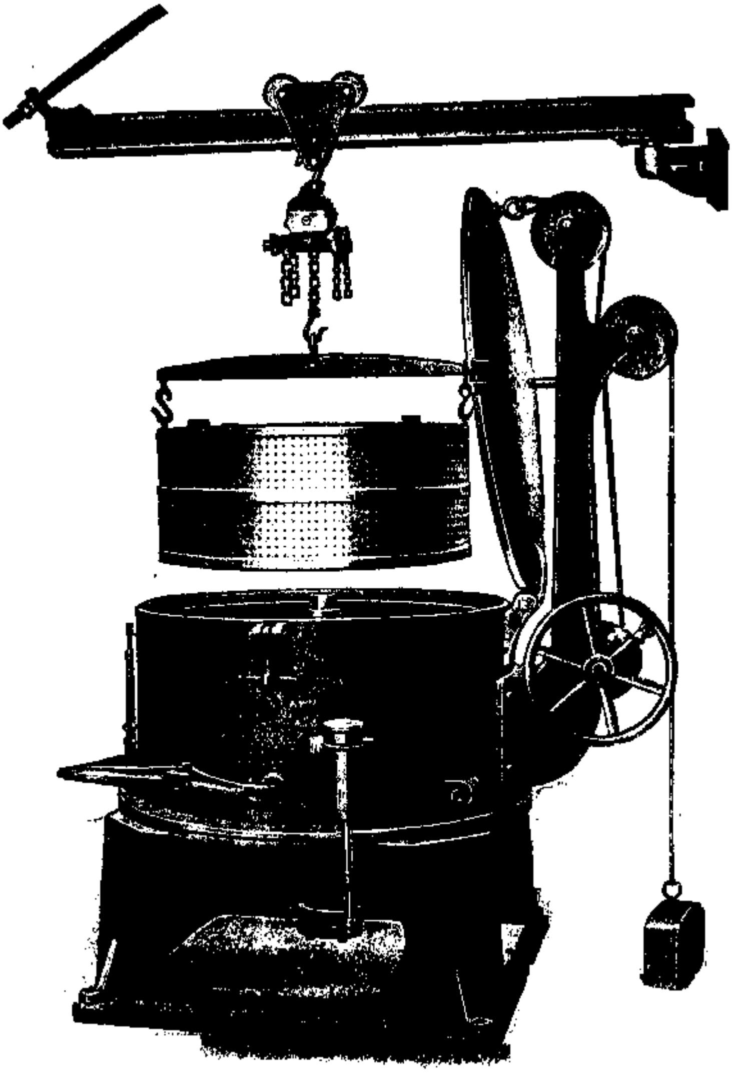

FIG. 6.—Turbine Centrifugal Fat Extractor, with lid raised and showing removable perforated steel Basket Also Swing Crane for lifting in and out the removable Baskets.

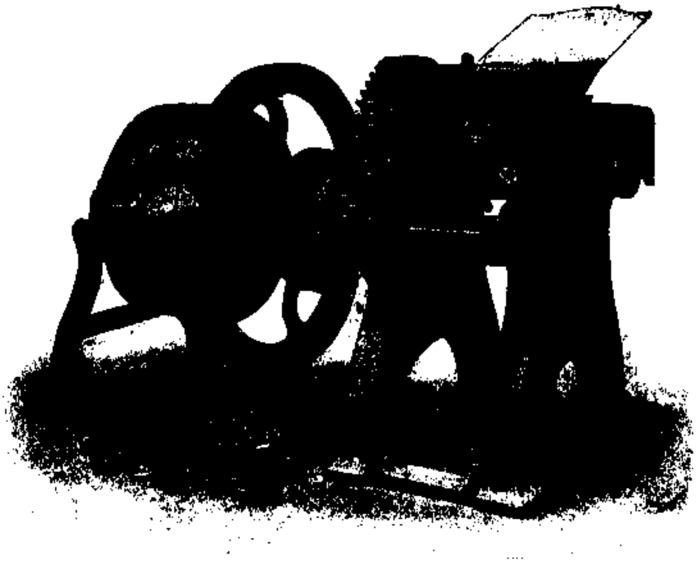

FIG. 7.—Bone-Crushing Machine.

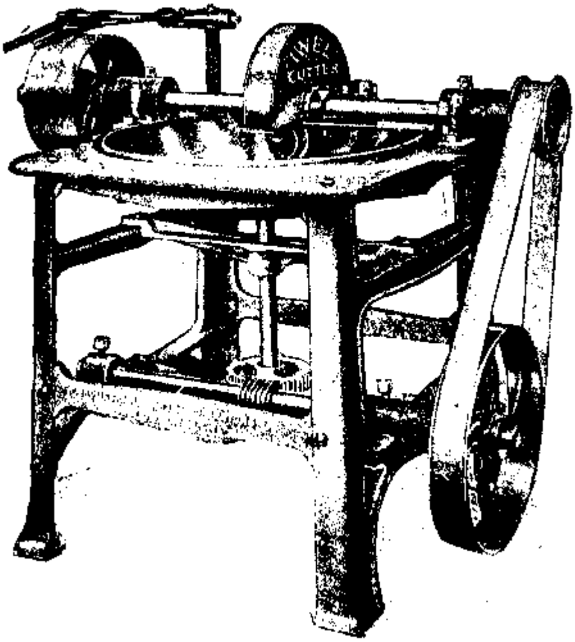

FIG. 8.—Slicing Machine for Organic Refuse.

through the dome D, thoroughly heating, permeating, and passing through the material.

The basket revolves with the perforated cage B at high speed and throws out the liquid fat with great force, and very thoroughly, from the solid residue, the fat being kept liquid by the steam. The liquid fat passes through the perforated cage B into the exterior chamber F, and thence through the outlet G, where it can be collected in any convenient vessel or led into a pipe line.

Bones are usually dumped apart, and before treating are broken up in a "bone-crusher," such as that illustrated in Fig. 7, and then placed in the melter, and finished off in the extractor, as above described.

It is an advantage also to slice up organic refuse before rendering, and this is usually performed in a machine such as that illustrated in Fig. 8. To the 2-in. high-speed shaft running in self-lubricating bearings are fitted four curved steel knives, conforming to the shape of the slowly revolving bowl which carries the material beneath the knives to be automatically cut to the necessary degree of fineness.

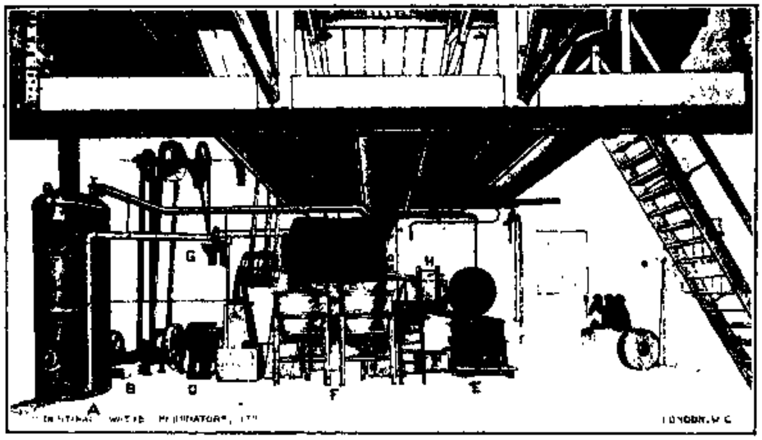

FIG. 9.—Complete Fat Rendering and Extraction Plant, for Kitchen Waste, Scraps, etc.

Fig. 9 shows a complete plant erected by the Industrial Waste Eliminators, Ltd., of London, for dealing with 20 tons of raw material per week. It deals with the cook-house waste from 15,000 men. Such a plant in 1916 cost approximately £1,800 and requires three men to work it. A is the steam boiler; B, the steam engine for driving the shafting, etc.; C, a bone-crusher; D, the fat melter above described; E, the turbine fat extractor; F, fat refining and melting tanks.

The waste from the army kitchens is first sorted out. Bones are dumped apart and treated separately as described below. All vegetable and green matter must also be separated from the meat trimmings, etc., because the green chlorophyll will pass into the rendered fat and colour it green, thereby destroying its commercial value.

The waste or "swill," comprising scraps of meat, etc., are placed in swill tubs, which are daily placed in motor lorries and transferred to the treating factory.

Here the swill tubs are transferred to an elevator and lifted to the floor above to be dumped into a capacious sink to drain.

After the swill has drained sufficiently it is passed into the fat melter D through a trap in the floor of the sink made like a hopper. The mass is heated in D for seventy to ninety minutes, and the fat rendered. Malodorous gases and moisture are withdrawn by the fan G, and conveyed beneath the boiler furnace and so burnt. In some cases the fumes are condensed.

The melted fat is run out from D into the refining or settling tanks F. The dry cooked meaty residue left in D is then raked out into the tank H and is then put through the turbine centrifugal extractors E, which removes quite 80 per cent. of the fat. The residue from E is of a rich chocolate colour, thoroughly cooked and quite inodorous. It is placed on floors to cool, and is sold as a pig-food.

It contains 6 per cent. of fat and a nutriment value of 125 units. The stuff, being sterilised and possessing excellent keeping qualities, commands a ready sale to farmers.

The dumped bones are treated separately. They are first gone over with a knife to remove all the meaty matter possible, next they are crushed in the bone-crusher C, and are then placed in D, where some fat is melted out, the bulk of the fat being removed by the centrifugal extractors E.

The treated swill and bones, which includes the meat meal from the bones, are ground and mixed in certain proportions, and sold as poultry food.

CHAPTER III

Recovery of Oil from Metal Turnings (Swarf) and Waste Rags, Etc., in Engineering Shops

CHAPTER III

RECOVERY OF OIL FROM METAL TURNINGS (SWARF) AND WASTE RAGS, Etc., IN ENGINEERING SHOPS

Contributed by E. A. Alliott, B.Sc. (Eng.), A.M.I.Mech.E.

Very large quantities of oil are now in use in engineering shops, for the purpose of cooling and lubricating cutting tools. These include animal oils, such as lard

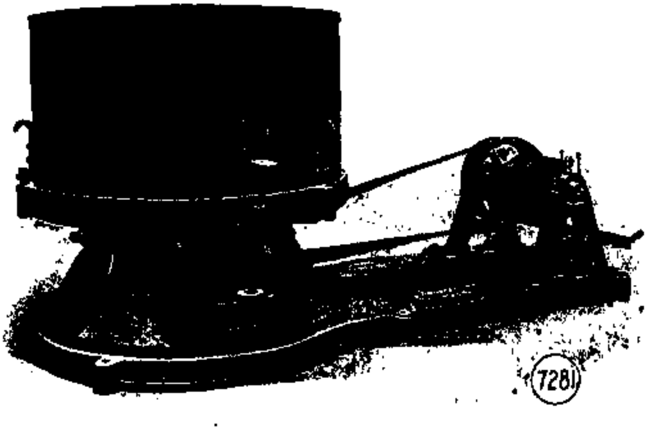

Fig. 10.—Centrifugal for separating Oil from Swarf.

(Manlove, Alliott & Co., Ltd.)

and tallow oil, neat's-foot oil, etc.; fish oils, such as sperm; vegetable oils, such as cotton seed, rape seed or colza; olive and resin oil, and mineral oils, such as petroleum. Drying oils are of little service, even in compounds, as they show a great tendency to gum.

Where possible it is now customary to employ emulsions, or mixtures of so-called soluble oils and water. A number of trade-marked oils of this description are on the market, and they give good service for cooling tools, where little lubrication is required. For work of great accuracy or high finish, and for use on automatic machines where water emulsions would tend to wash the oil out of the bearings, or where long chips or turnings are produced rendering lubrication essential, pure oils, or oil compounds, are necessary. Lard oil, and mixtures of lard and mineral oil, are most commonly used. Owing to the high price and present scarcity of these lubricants, economy in use is most essential.

The largest source of waste is the retention of oil in the metallic swarf, turnings, borings, or cuttings from the machines, also in the cotton waste, sponge cloths, rags, etc., used for wiping, and in sawdust, which is often put on the floor for mopping up any spilled oil.

Oily steel or brass swarf will retain from 10 per cent. to 30 per cent. of oil, depending on the class of swarf and viscosity of the oil, while waste and rags may contain double this amount.

The best method of treatment is undoubtedly to subject them to high centrifugal force, by which the draining effect of gravity is multiplied several hundredfold. In properly designed machines, practically the whole of the oil may be recovered.

A type of machine suitable for large installations is shown in the illustrations (Figs. 10 and 11). It is fitted with a perforated steel plate basket, having a pair of trunnions on the side. At the close of an operation the basket may be lifted out of the machine by the shackles, and can then be taken by an overhead runway to the discharge dump, where the contents are tipped out. For ease in emptying, the upper lip of the basket is made conical in form. Two rings containing mercury are fitted to the bottom of the basket, and these help to compensate for any inequality in loading the machine. The dome of the basket fits into a taper cone on the revolving spindle, the taper being adjusted to give ease in removal of the basket, together with sufficient grip to drive it. The spindle runs in a pivoted centre bracket, retained in position by rods fitted with springs and rubber buffers, so that the basket may revolve around its own centre of gravity, and does not jar the foundations when the load is out of balance.

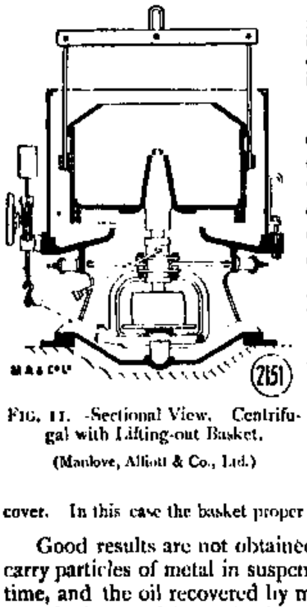

Fig. 11.—Sectional View. Centrifugal with Lifting-out Basket.

(Manlove, Alliott & Co., Ltd.)

Steaming.—*Steaming* is not essential or even desirable when dealing with *swarf*. The latter drains quite well at ordinary temperatures, and very little extra can be obtained by steam, which condenses and has to be separated from the oil coming from the machine. Where *rags* and *sponge cloths* are being treated, steaming undoubtedly helps to bring the oil away quicker, and less is left in the treated material.

The machine described above may be fitted with a cover and steam pipe leading to the interior of the basket, and comparatively little steam is required for the purpose. Another type of machine has a fixed spindle, and is driven by a steam turbine, the blades of which are secured to the underside of the basket (see Fig. 5). After passing through the turbine the steam enters the basket, and is led away to exhaust. The extracted oil and condensed steam leave by a trapped outlet, while the pan is fitted with a steam-tight cover. In this case the basket proper is not removable, but is provided with a loose inner cage.

Good results are not obtained with tools lubricated by oils or emulsions which carry particles of metal in suspension. Lubricants which have been in use for some time, and the oil recovered by means of such separators as described, are found to contain fine particles and spicules of metal which depreciate their usefulness. Very often but little attention is paid to this factor. A filter may be fitted in the circulating arrangements to each separate machine tool, and the oil from the centrifugals dealt with separately, but the best plan is to instal a central oil cleansing plant to which the oil continually returns both from machines and separators, and from which it is sent back clean. The usual means employed are settlement or filtration, or a combination of both. Heating is often resorted to in order to accelerate settlement. Temperatures in practice vary from about 100° F. up to well over 200° F. Plain settlement involves little attention, but a number of tanks are provided, which are filled in rotation. The oil is allowed to stand for six to eight days prior to decantation, and hence a large amount of oil has to be held in reserve, while the space required is fairly considerable. Filters and filter presses are in use, and if the oil is passed through a filter press in which a layer of diatomite has been deposited, the purified oil will often be a better product than when originally bought. The rate of filtration is, however, very slow. Generally speaking, it is usual to settle the oil before filtration to remove the coarser particles. There are on the market a number of devices in which both settlement and filtration are employed. In certain cases magnetic separation is used.

A mechanical subsider has recently come into use in which centrifugal force is employed to increase the rate of settlement, while the settled particles are washed free from oil by passing through a layer of water. Loss of oil is thus very greatly minimised.

The machine is built on the lines of an ordinary centrifugal, but the basket is not perforated, and is filled at the commencement of the operation with a suitable quantity of water to form an almost vertical wall within a little distance of the rim of the basket when the latter is revolving at high speed. Oil is run into the basket from a container, and fills the space between the water and the rim, flowing over the latter to the outer pan, where it is collected and run to a container through a spout.

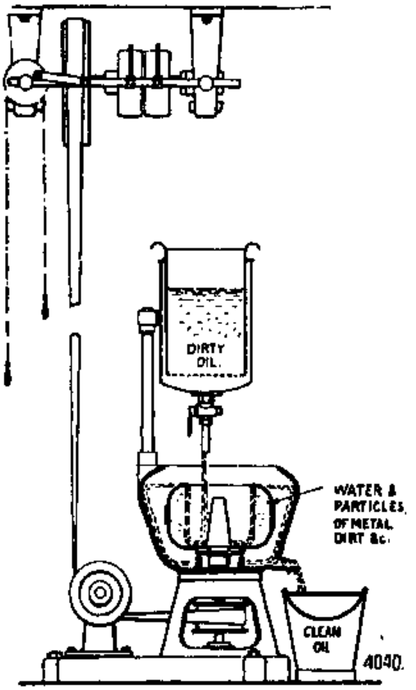

FIG. 12.—Spratt's Patent Oil Subsidiser for Separating fine metallic Particles from Oil.

(Manlove, Alliott & Co., Ltd.)

Any particles of dirt or metal of a greater specific gravity than the oil pass into the water, which washes off any entrained oil, and collect on the sides of the basket. The latter is cleaned about once a day, when more water is run into the basket to displace the remaining oil. The basket can then be lifted out by hand, cleaned, and replaced in a few minutes. The working is practically continuous, little space is required, and a minimum of oil need be kept in circulation.

Sterilisation is sometimes resorted to in order to prevent development of sores, etc., which are liable to appear on the hands and arms of workers who are employed on machines on which a large quantity of lubricant is used.

Such sores and rashes are produced by plugging of the glands at the roots of the hairs on the arms and hands of workers; and by the injurious action on the skin of fine metallic particles suspended in the oil, causing abrasions which permit the entrance of germs. The remedies are strict attention to the cleanliness of the worker, and the adoption of efficient means for freeing the oil from minute particles of metal. The oil should be as free as possible from fatty acids, and may be sterilised.

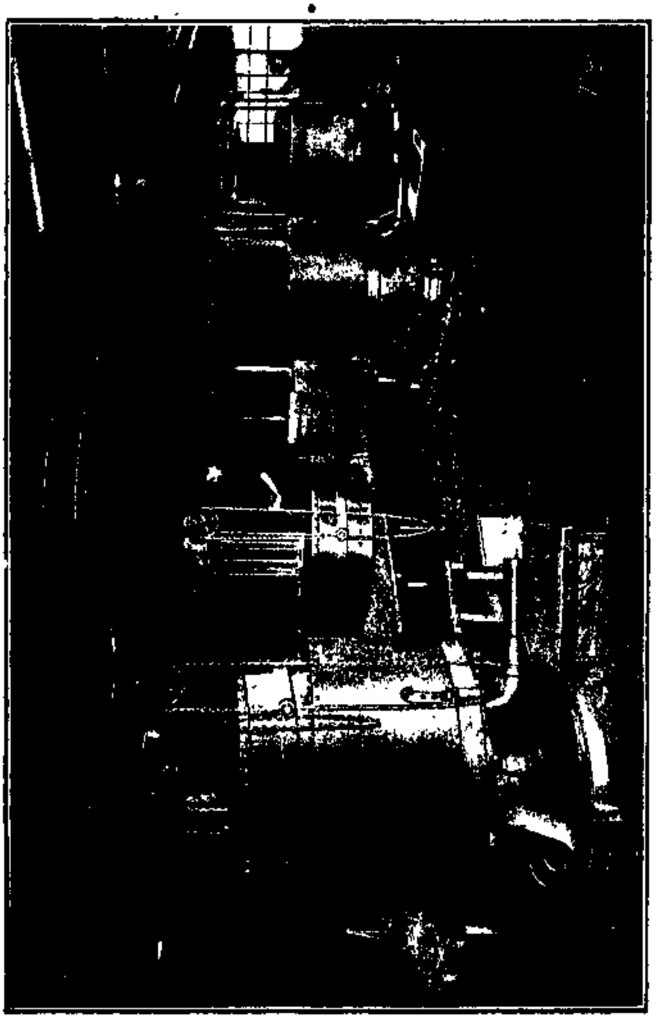

FIG. 13.—Swarf De-oiling Plant at the Works of the Hoffmann Manufacturing Co., Ltd., Chelmsford.
(Centrifugals by Manlove, Alliott & Co., Ltd.).

Some investigators report that they get good results by heating the oil to a temperature of 140° F. for twenty minutes. This does not, however, appear to be sufficient to destroy spores, and a temperature of, say, 240° F. would be better. Mixtures of lard oil and petroleum are said to develop a powerful germicide after use, while some managements add about 2 per cent. of carbolic acid to the lubricant. The value of sterilisation is not, however, finally proved. To get good results, not only the oil but the pans, containers, and pipes would need to be treated.

One of the largest swarf de-oiling plants in this country is at the works of Messrs The Hoffmann Manufacturing Co., Ltd., Chelmsford. It consists of three 40-in. self-balancing centrifugals with lifting-out baskets. The swarf is collected from the

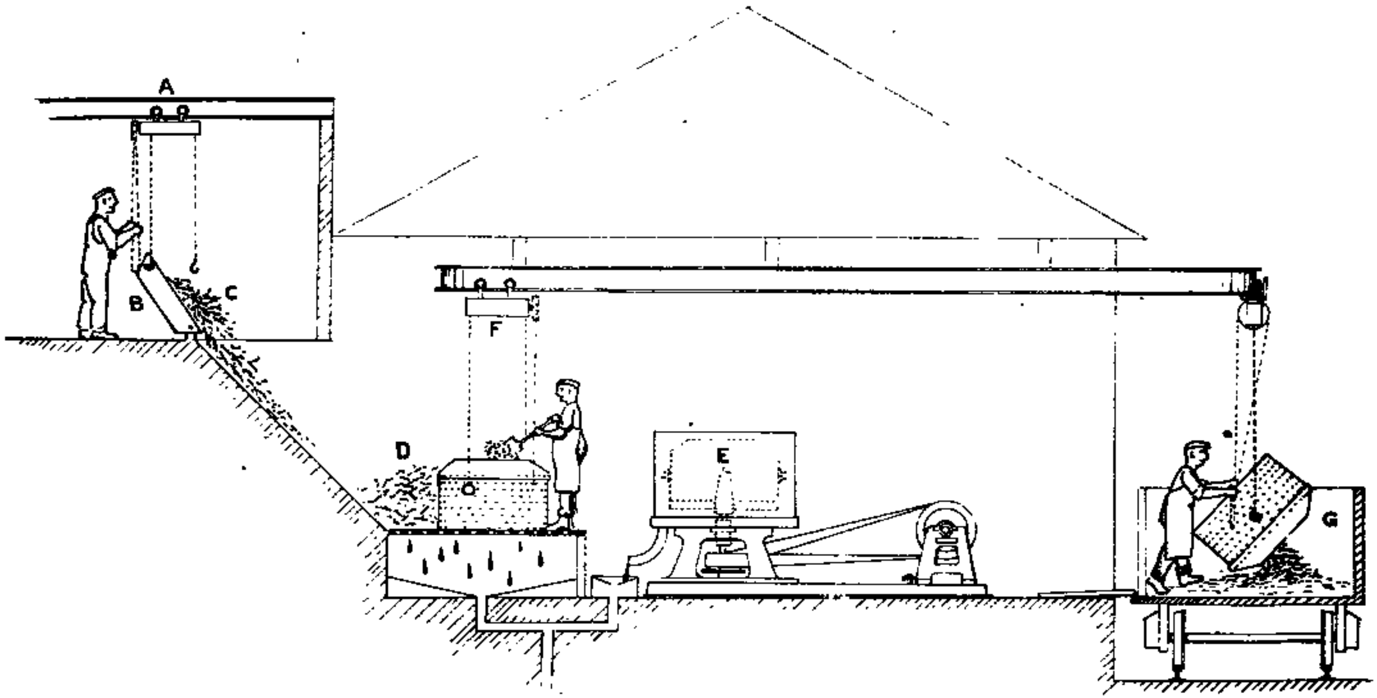

FIG. 14.—Arrangement of Swarf De-oiling Plant at the Works of the Hoffmann Manufacturing Co., Ltd.

(Centrifugals by Manlove, Alliott & Co., Ltd.)

machine shops in special steel plate trollies, fitted with rollers, which are pushed from machine to machine. An overhead runway leads to the de-oiling plant, which abuts on the railway sidings. The trolly, when filled, is hooked to chains attached to the overhead runner. The rail rises slightly, so that the trollies after being pushed a few yards are lifted clear off the ground, and are easily conveyed to their destination. On arrival they are tipped into a grid over which the swarf is pushed. The smaller pieces fall through on to the charging platform, while the larger pass to a machine which cuts them into more convenient lengths for handling. The interior of the extractor house is provided with overhead runways, for the easy moving of the baskets between the charging floor, the machines, and the discharge platform. The machines are provided with spare baskets, which are filled by spade on the charging floor while the previous charge is being whizzed. The discharge platform is arranged with a shoot, so that the de-oiled swarf may be loaded direct into a railway wagon.

The swarf is not steamed, but provision is made for keeping the plant reasonably warm in cold weather, to prevent congealing of the oil. The charging floor and working floors are provided with drain gutters for the oil, and these are fitted with specially designed grids or covers to prevent them becoming choked with swarf. Below the de-oiling house is a settling room, provided with six tanks in which the dirty oil is settled. Each tank holds about 1,000 gallons, and when full is allowed to stand from six to eight days before decantation. A special tank is provided for separating any water which may have become mixed with the oil. The same room contains storage tanks for fresh oil, which is brought in to make up wastage.

The machines make two to three operations per hour, according to the amount of oil in the turnings and their nature. One set of experiments showed that a load of short chips was 5 cwt., from which 20 gallons of oil were recovered. For long chips the load weighed 2 cwt., and the recovered oil was 2¼ gallons. These figures are on the low side for oil estimation, as the chips had been allowed to drain during the week.

In 1917 this plant, working 9½ hours a day, 6 days per week, dealt with 2,885 tons of oil and swarf, from which 877 tons of oil were recovered.

The same firm have also a separate installation for treating their oily rags and sawdust, consisting of a turbine-driven centrifugal, two all-metal washing machines, and a drying room. Some 10 cwt. of rags are treated weekly, from which 80 to 120 gallons of oil are recovered. In addition to this, overalls, etc., are treated, and new rags are steamed in the machine with a view to sterilisation before use. Further machines of each type are in process of installation.

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CHAPTER IV

Manufacture of Fish Oils, Fish Meal, and Fish Guano

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BENGAL

CHAPTER IV

MANUFACTURE OF FISH OILS, FISH MEAL, AND FISH GUANO

Fish Oils are obtained from all parts of the body of common fish—such as sardine, salmon, sprat, herring, menhaden, etc., by boiling.

Menhaden Oil is prepared from the heads and intestines of fish, especially of the menhaden or mossbanker of the Atlantic coast of America; it is used in the leather, paint, and rope trades.

For **Sperm** and **Arctic Sperm Oil** see under **Liquid Waxes.**

The best sorts of **Cod Liver Oil** are prepared by heating the livers (taken from the fish brought ashore alive and treated the same day) of the cod fish in steam-jacketed vessels, when the cell membranes burst and the oil exudes. Inferior qualities are obtained by treating the putrid livers in a similar way; although unfit for medicinal purposes, it is largely used in the leather industry (see **Dégras**).

It is advisable to render in a vacuum in an autoclave fitted with stirrers. The vacuum heating reduces the temperature of rendering, with the result that the oil is improved both in colour and odour. In the case of livers which are in a state of partial decomposition the boiling under vacuum has the effect of sweetening the oil considerably and improving the colour.

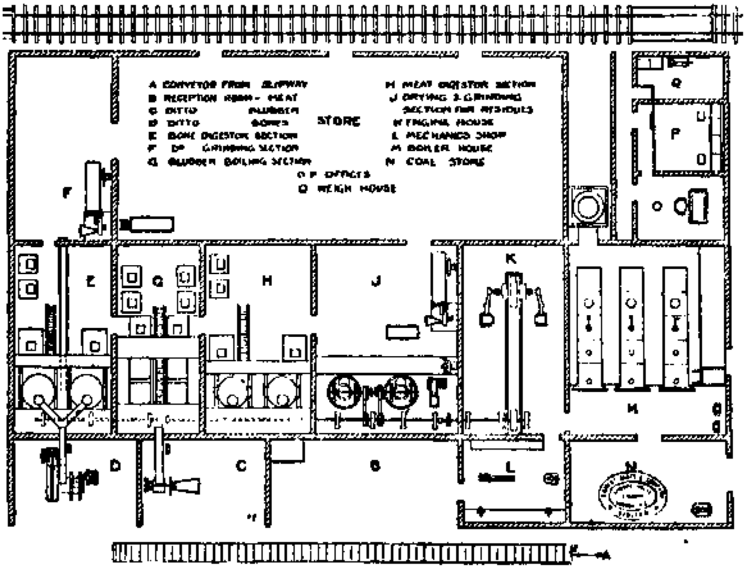

FIG. 15.—Factory for Manufacture of Whale and Seal Oil.

(Scotts, Kingsway House, London.)

Seal and whale oil are extracted from the blubber of the animals, sometimes on board ship itself, but more often in "trying" stations situated in Finnmarken, on the Lofotes, and in Iceland. The blubber is stripped clean from the flesh immediately after the arrival of the ship, cut into strips, chopped in mincing machines, delivered into melting pans, and boiled with steam.

Fig. 15 shows a factory for extracting whale and seal oil, erected by Scott & Son, of London.

In modern works it is more economical to extract the oil by solvent, as a better and more complete yield of oil is thus obtained.

This is now done in plant similar to that described below under **Fish Offal.**

Fish oils are *used* for tempering steel, in leather manufacture, for soap and candles.

TREATMENT OF FISH OFFAL TO RECOVER OIL. MANUFACTURE OF FISH MEAL AND FISH GUANO

LITERATURE

C. R. Growther.—"Fish Meal as a Food for Live Stock." *Jr. Board Agric.*, 1919, xxvi. 480.

F. C. Weber.—"Fish Meal: Its Use as a Stock and Poultry Food." United States Department of Agriculture, Bulletin No. 373 (1916).

F. G. Ashbrook.—"Fish Meal as a Feed for Swine." United States Department of Agriculture, Bulletin 610 (1917).

A. M.—"Fish Meal: Its Composition and Value as a Feeding Stuff for Pigs, Poultry, Cattle, and Sheep." The Aberdeen University Press, Ltd., Aberdeen (1917).

In the fishing ports of Scotland and the east of England very large quantities of fish offal occur, such as heads, rotting fish, waste parts, etc. This was formerly thrown away, and often became a source of serious nuisance. At the present time, and to an increasing extent, this offal is worked up and utilised.

The total value of the fish landed in British ports in 1913 was £14,229,000, representing 1,223,000 tons. One-third of this represents herrings which are too rich in oil to be worked up directly to fish meal, so that the oil has to be extracted first before the residue is usable. In order to make the fish pack well and save weight in carriage as much as one fourth of the weight of the fish is cut off, and hence the large residues left.

Three products are obtainable from fish offal:—

(1) **Fish Guano.**—An excellent fertiliser for the land.

(2) **Fish Meal.**—An excellent feeding stuff for cattle, pigs, and poultry.

(3) **Fish Oil.**—Mostly herring oil.

Process of Manufacture

The fish remains are placed in a "cooker," Fig. 16, which consists of a flat-topped, semi-cylindrical vessel, steam-jacketed on the lower half, and provided with steering gear, a discharging valve at the bottom, and a charging door on the top. The vessel is connected to a vacuum pump, and the fish remains heated under vacuum. The offensive vapours pass off, are condensed, and are usually passed through the boiler furnaces, so as to be burnt, and thus rendered inodorous. Some works, however, pass the gases through coke beds down which water is passing.

In the case of herring offal and other very oily fish, the oil separates out and is removed (after the cooking process has been completed) by breaking the vacuum, opening the hinged door on the top, and scooping out the separated oil with balers.

The oil thus separated is filtered, and sold as a fish oil of good quality. The remains are now discharged by the door at the bottom of the cooker, and the dry mass powdered in a grinding machine and sold as a fertiliser under the name "fish guano."

When the fish is of good quality and fresh it forms "fish meal," and is an excellent cattle food. "White fish meal" can even be used for human food.

When **fish oil** is the product desired it is highly advisable to extract the oil by means of solvents, as a much more complete separation is thus attained.

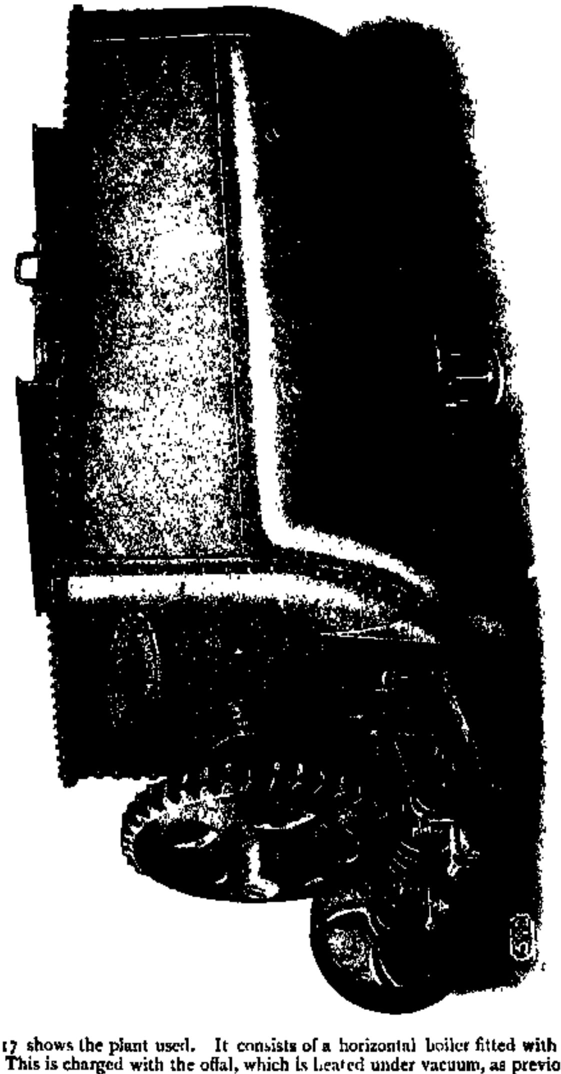

FIG. 16.—"Cooker" for Fish Offal.
(Scotts, Kingsway House, London.)

Fig. 17 shows the plant used. It consists of a horizontal boiler fitted with stirrers and steam-jacket. This is charged with the offal, which is heated under vacuum, as previously described, until the offensive odours have escaped and the material is dry.

The mass is then submitted to the action of hot benzine and benzine vapour in the manner described below under "solvent extraction" of vegetable oils.

The benzine rich in oil is pumped away to the still (shown on the right) and is there distilled away from the fat in the usual way.

The residue of fish meal left in the extractor is finally steamed to remove benzine, and the product removed, ground as before, and sold as fish meal, or as a fertiliser.

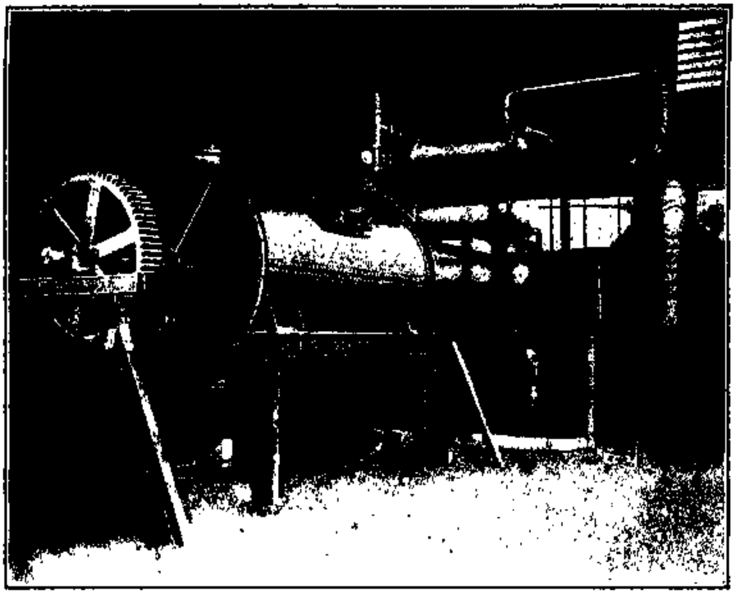

FIG. 17.—Solvent Extraction Plant for Fish Offal.
(Scotts, Kingsway House, London.)

Chemical Composition of Fish Meals

The following table shows the results of analyses of typical fish meals:—

ANALYSES OF WHITE FISH MEAL.

	1.	2.	3.	4.	5.	6.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Moisture	11.07	12.94	14.90	18.45	...	...
Nitrogen	8.93	9.59	9.31	9.12	9.12	8.93
Equal to Ammonia	10.84	...	11.31	...	11.07	10.84
Salt	2.24	2.44	...	3.13	4.65	4.81
Oil	6.23	3.65	3.00	6.53	5.16	5.92
Phosphate of Lime	19.88	17.23	18.24	...	19.12	20.28

The following represents an analysis of the ash:—

Insoluble	0.50
Iron and aluminium (Fe_2O_3, Al_2O_3)	0.97
Phosphoric acid (P_2O_5)	35.32
Calcium (CaO)	26.86
Salt (NaCl)	25.83
Magnesium (MgO)	3.13

Herring meal differs in composition from white fish meal. The following are typical analyses:—

ANALYSES OF HERRING GUANO.

	1.	2.	3.	4.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Moisture	11.52	14.83	15.68	9.79
Nitrogen	8.03	...	9.33	9.04
Equal to Ammonia	9.75	10.33	11.33	10.98
Phosphoric acid	3.54	...	3.93	...
Equal to Phosphates	7.72	...	8.57	13.24
Oil	3.76	5.00	6.04	3.45
Salt	22.73	17.96	6.77	9.25

	Pure Herring Meal.	Herring Guano.
	Per Cent.	Per Cent.
Moisture	15.35	15.82
* Albuminoids	58.13	57.94
Oil	4.99	4.92
** Ash	18.64	18.74
Combined water loss and undetermined matter	2.89	2.58
	100.00	100.00
	Per Cent	Per Cent.
* Containing nitrogen	9.30	9.27
Equal to Ammonia	11.29	11.25
** Containing total phosphates	10.06	9.58
Salt	8.27	9.06

It will be seen from these analyses that the composition of fish meal is very variable. Growther (*loc. cit.*) gives the following table:—

	Range of Variation.
	Per Cent.
Moisture	7.7 to 18.1
Albuminoids (protein)	51.1 ,, 63.1
Oil	1.3 ,, 6.7
Ash	20.8 ,, 28.0
(Includes calcium phosphate)	16.6 ,, 20.6
Salt	0.6 ,, 5.3
Carbohydrates, fibres, etc.	0.3 ,, 4.2

It will be seen that fish meal is very rich in albuminoids, mineral matter, and oils. It has a high food value, and has been used with success for feeding dairy cows, using 1 lb. per cow per day, in the form of a mixed ration.

Since fish meal contains only a small proportion of carbohydrates, it can only exercise its full effective value **when used mixed with other feeding stuffs containing an abundance of carbohydrates.**

Fish meal should not form more than one-eighth of the total dry food consumed.

It must not be too rich in **fish oil**, otherwise a fishy taint may develop in pork or bacon produced with its aid. Hence the fish meal, fish guano, and fish oil manufacturers have agreed to produce a meal from white fish only (*i.e.*, without herrings, etc.), to be sold as "White Fish Meal," and to conform with the following limits as to composition:—

Albuminoids	not less than 55 per cent.
Phosphate of lime	,, ,, 16 ,,
Oil	not more than 5 ,,
Salt	,, ,, 4 ,,

The meal should be light brown in colour, free from offensive smell, and if the moisture content does not exceed 10 per cent. it may be kept for long periods on a wooden floor in a dry store.

For pigs and poultry fish meal should only have a minute proportion of salt.

Fish meal is, at present, one of the cheapest foodstuffs as the following table shows:—

ANALYSES AND PRICE PER TON OF VARIOUS FEEDING STUFFS.

(Extract from "The Farmer and Stockbreeder," 18th August 1919.)

Foodstuff.	Dig. Protein.	Dig. Oil	Dig. Carbo-hydrates.	Food Units.	Price per Ton.			Price per Dig. Food Unit.	
					£	s.	d.	s.	d.
Fish meal	54	4	..	145	22	0	0	3	0
Linseed	18	35	20	153	56	0	0	7	3
Bombay cotton cake	13	4	21	65	20	0	0	6	2
Egyptian cotton cake	15	5	20	72	22	0	0	6	1
Locust bean meal	4	1	69	81	22	0	0	5	5
Peas	17	1	50	97	26	10	0	5	5
Beans	20	2	48	99	26	10	0	5	4
Chinese beans	20	2	48	101	27	0	0	5	4
Rice meal	7	10	38	79	21	0	0	5	4
Linseed cake	27	9	30	120	26	0	0	4	4
Maize germ meal	9	6	61	99	21	10	0	4	4
Dried grains	14	7	33	84	17	10	0	4	2
Barley	8	2	60	83	17	4	0	4	2
Oats	7	4	47	75	15	16	0	4	2
Coco-nut cake	16	8	41	102	21	0	0	4	1
Palm-nut cake	12	8	39	90	18	10	0	4	1
Malt culms	11	1	39	70	14	10	0	4	1
Wheat	8	1	64	84	16	16	0	4	0
Decorticated cotton cake	34	8	20	126	24	0	0	3	10
Sharps	12	4	53	84	16	0	0	3	10
Treacle	...	...	60	60	11	10	0	3	10
Maize gluten feed	20	9	48	122	23	0	0	3	9
Distillery grains	19	10	29	101	18	0	0	3	6
Maize	7	4	66	94	16	0	0	3	5
Bran	11	3	45	77	13	0	0	3	4
Ground-nut cake	45	6	21	145	23	0	0	3	2

The lower grade fish meals, which are of a brown colour, and made from fish remains which are not quite fresh, should not be used for cattle food, but has (as indicated in the above analysis) a high value as a manure.

For further details regarding **fish meal** see the above-quoted literature.

Acknowledgments.—The author wishes to thank Mr Fred. A. Lass, of the North Shields Fish Guano and Oil Company, for much valuable information and help in preparing the preceding section.

CHAPTER V

Manufacture of Vegetable Oils by Pressing

CHAPTER V

MANUFACTURE OF VEGETABLE OILS BY PRESSING

Summary and Description of Machinery Employed

Vegetable oils and fats are obtained from oil-bearing substances (usually seeds) by two distinct processes :—*

(*a*) By pressing in hydraulic presses.
(*b*) By extracting with volatile solvents.

Oil Extraction by Pressure.

Four distinct operations are usually performed :—

(1) The seed is crushed or ground in special machines so as to break the oil cells.

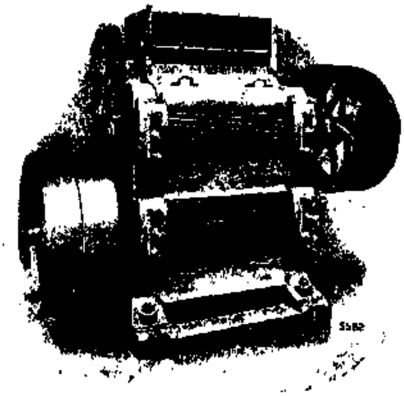

Fig. 18.—Preliminary Reduction Machine for Copra.
(Manlove, Alliott, of Nottingham.)

(2) The ground seed is heated so as to facilitate the flow of oil and to coagulate the albumen.

(3) The product is now gently pressed in a moulding machine to prepare it for the hydraulic press.

(4) Finally, the seed is conveyed to hydraulic presses and the oil expressed.

We will firstly describe the machinery used in each of these operations before going on to describe the treatment of the individual seeds.

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* For blocks and illustrations of machinery employed in seed-crushing, the author has pleasure in thanking Messrs Rose, Downs, & Thompson, of Hull, and Manlove, Alliott, of Nottingham.

Preliminary Reduction Machines

Certain oil seeds, such as copra, palm kernels, ground nuts (arachides), etc., usually require preliminary reduction before it is possible to finally grind or roll in readiness for pressing.

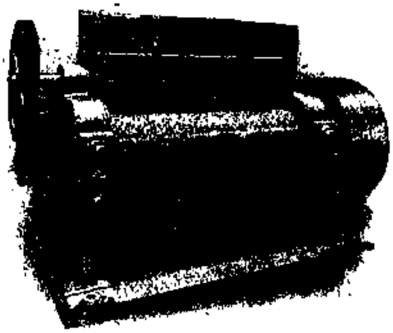

FIG. 19.—Preliminary Reduction Roll for Castor Seed.
(Manlove, Alliott, of Nottingham.)

These machines generally take the form of horizontal rolls, with either one, two, or three pairs of rolls, suitably grooved, as may be found necessary.

Copra is usually delivered to the factory in pieces of considerable size, and to reduce this it is necessary to pass through two machines, each containing two pairs of rollers, as illustrated by Fig. 18.

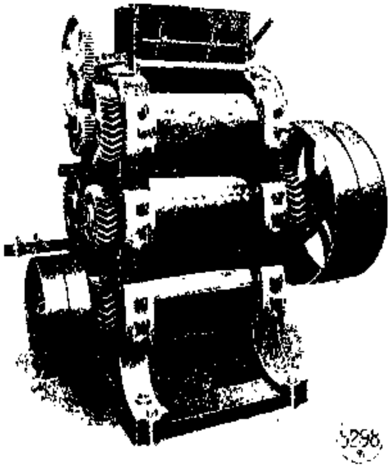

FIG. 20.—Preliminary Reduction Rolls for Oil Extraction by Solvents.
(Manlove, Alliott, of Nottingham.)

The rolls are constructed of chilled cast iron, each pair being independently driven, the two rolls running at unequal speeds; whilst in the first machine the rolls are coarse grooved, in the succeeding machine the grooves are finer.

Fig. 19 shows a pair of single rolls, which are used for the reduction of castor seed or similar seeds of a soft nature, but of such a size as to prevent their being passed directly to the finer crushing rolls.

In many factories castor seed and ground nuts are pressed twice, and it is customary to deliver the seed directly from these rolls to the heating kettle (described below). The construction of the rolls is similar to those previously described, except that the rolls are not equal speeds, the cutting rolls not being necessary when rolling seeds of a softer nature.

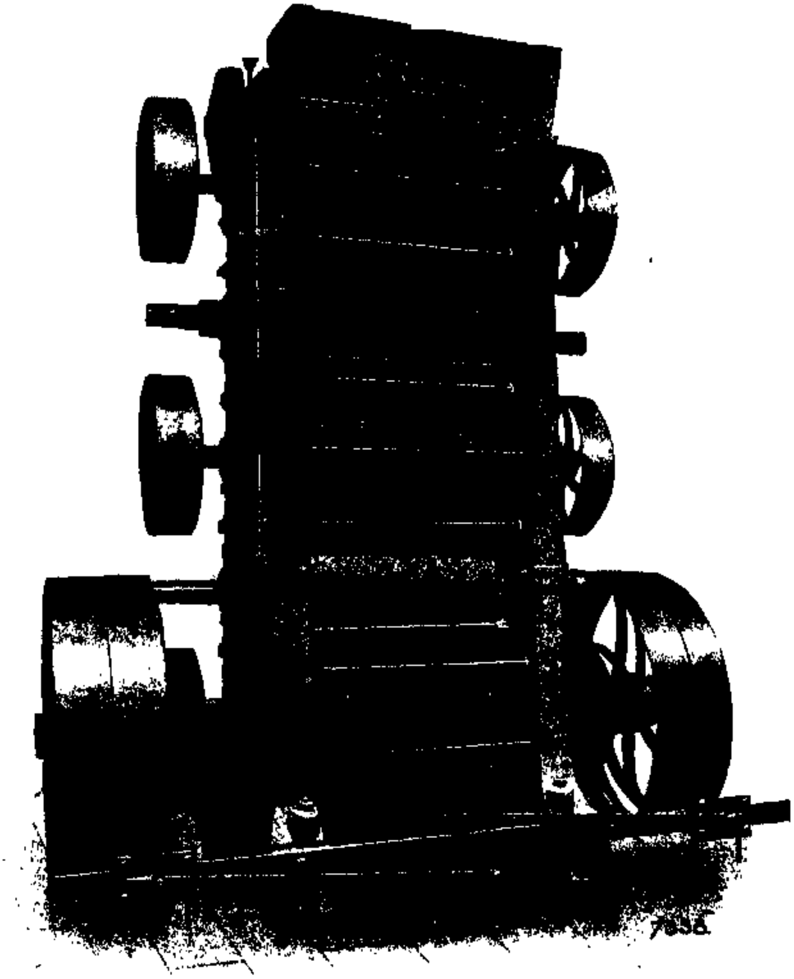

FIG. 21.—Anglo-American Rolls for final Treatment of Seeds.

Fig. 20 illustrates a set of rolls with three pairs of rolls, the two upper ones being grooved and the lower pair smooth.

These are for use when the seed requires to be delivered in a flaked condition, and are very generally in use in factories where the oil is obtained by the use of solvents. In construction the rolls are similar to those previously described, except as regards method of driving, the two upper pairs of rolls being driven by means of gearing by one belt, each pair of rolls running at different speeds, whilst the lower pair of rolls is separately driven, and each roll runs at the same speed to avoid any cutting action.

Final Crushing Rolls

For the final treatment of oil seeds, rolls of the Anglo-American type are used. These consist of five chilled rolls carried in vertical side frames, the rolls resting face to face upon one another, and thus applying a greater pressure to the seed as it passes between each roll, which it is obliged to do owing to the arrangement of the guide plates and scrapers.

Fig. 21 illustrates a set of Anglo-American rolls of this nature specially designed for the treatment of oil seeds yielding edible oil. They are 24 in. diameter by 42 in. long, each roll being constructed of chilled cast iron, the three upper rolls being suitably grooved. Special provision is made whereby the rolls can be adjusted as regards pressure, in order to ensure an even flow of meal; they are driven at both ends, the upper rolls being driven from the shaft which passes through the lower rolls. The two intermediate rolls are not driven, the power being applied by friction only, thereby allowing for a certain slip which assists in the flaking of the meal and the production of a fine product.

In the set of rolls illustrated provision is made whereby the rolls can be withdrawn without dismantling the feed hopper, one-half of the side frame being removable, thus allowing for the rolls to be withdrawn sideways instead of lifting over the top of the frames, as is generally done.

All Anglo-American rolls are constructed on this principle, but different size and weight of rolls are used, according to the nature of the seed being rolled.

Decorticating Machinery

Certain seeds when they are delivered to the factory are covered with shell or skin, which contains no oil, and whilst many seed-crushers prefer to crush this seed whole rather than be put to the trouble and expense of removing this shell, it is certainly desirable that when the greatest possible yield of oil is required the shell should be removed.

In England cotton seed is usually ground and pressed without having the outer husk removed, whilst in America and India decorticators are usually found in most up-to-date oil mills.

A decorticating machine usually consists of a pair of rolls set at such centres as to slightly squeeze the seed and crack the outer husk or shell, from whence it is delivered on to a shaking separator, which is vibrated in such a manner as to remove the kernel from the husk. On leaving the separator it is delivered into a shoot, through which passes a blast of air from an aspirating fan. The husk, being of a lighter nature than the kernel, is carried away by the air blast, the kernel being delivered free from husk at the side of the machine.

Castor seed when thus treated is suitable for obtaining the highest quality of medicinal oil.

A somewhat similar machine is used for the decortication of ground nuts, with the addition of a revolving screen for removing the inner red skin. Some manufacturers also provide a brushing machine, the seed passing between revolving brushes to complete the removal of the red skin. Many manufacturers, however, prefer to crush ground nuts without the removal of the husk, as, although this contains no oil, it has a certain feeding value.

Use of Disintegrators

Fig. 22 illustrates a disintegrator which is often used for the reduction of copra, palm kernels, or any particularly hard seeds which may be under treatment. This machine in no way resembles the preliminary reduction machinery previously described, being essentially a breaking machine. The machine is constructed with massive cast-iron outer casing fitted with inner gratings or liners, through which the seed is forced by the action of a revolving disc fitted with beaters.

The machine runs at a very high speed, the beaters revolving at a speed of about 2,000 revs. per minute, and the broken seed is delivered in fine particles.

In order to ensure an even grade of output an automatic feed device is usually provided, as unequal feeding has a tendency to choke the machine, necessitating considerable trouble in clearing the obstruction. The one drawback to the use of this machine, in lieu of rolls for the preliminary reduction of oil-bearing seeds, is that the meal is delivered in granular form, and the oil cells are not sufficiently bruised to ensure the maximum yield of oil.

Meal Heating Kettles

After the seed has been satisfactorily rolled and reduced to meal, it is necessary, in order to express the oil by hydraulic pressure, to thoroughly moisten and heat the meal to a suitable temperature to allow the oil to flow freely. For this purpose it is customary to deliver the meal to a heating kettle constructed either of cast iron or steel, steam-jacketed, and fitted with a meal moistening device and agitating gear, in order to ensure the whole contents of the kettle being equably heated and moistened.

Different seeds require different temperatures, and as in such cases it would necessitate keeping the meal in the heating kettle a considerable period of time to obtain the necessary heat, it is preferable to have two kettles, one mounted above the other, the first of which receives the seed and gives preliminary treatment, the second completing the process and allowing for a considerably greater output than would be the case with a single kettle.

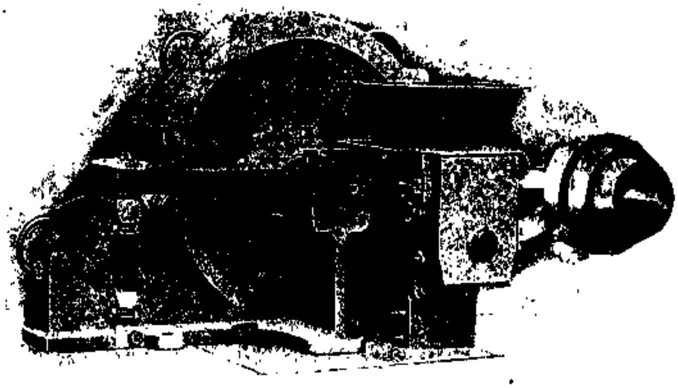

FIG. 22.—Disintegrator for Copra, Locust Beans, etc.

(Manlove, Alliott, Nottingham.)

In the treatment of palm kernels it is desirable that two kettles should be used for another important reason, viz., to allow the majority of the inherent moisture contained in the seed being driven off from the meal before the moisture is finally added to assist the flow of meal. This small detail has a very considerable effect as regards the yield of oil.

Each heating kettle is provided with an automatic mouthpiece which is closed when the strickling box, which is the usual means adopted of withdrawing the meal from the kettle, is removed from its position on the slide plate, and opens when the strickling box is replaced in position in order to receive its charge of meal.

Cake Moulding or Forming Machines

Seeds containing not more than 35 per cent. of oil can be pressed in Anglo-American hydraulic presses with open plates, and in order to allow the greatest possible number of cakes being placed in the press, and further, to assist the meal in retaining its form when placed in the press, cake moulding or forming machines are used. These consist essentially of a mould frame, which is hinged in order to allow a tray being placed either upon a sliding frame which carries the tray and meal, which is folded in a wrapper, on to the pressing ram; or it may be so arranged that the table which supports the tray is a continuation of the ram itself.

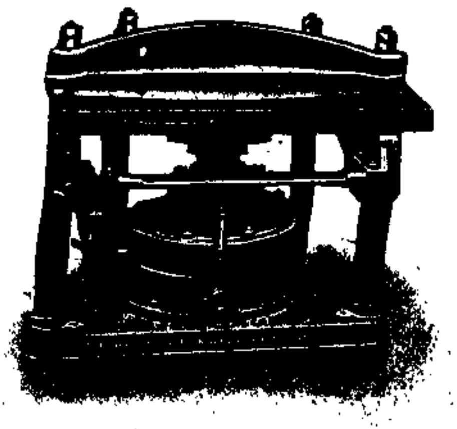

FIG. 23.—Cake Moulding Machine with Steam Cylinder.

The pressure may be applied by means of hydraulic or steam pressure, and is so regulated as to apply pressure up to such a point as to ensure the meal being compressed into reasonable limits, whilst avoiding any extraction of the oil.

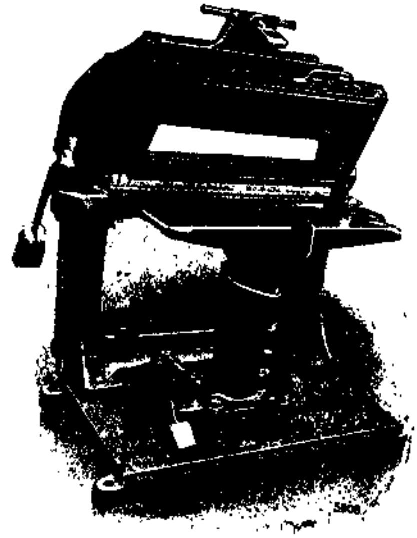

FIG. 24.—Cake Moulding Machine with Hydraulic Cylinder.

Fig. 23 illustrates a machine of this nature with steam compressor cylinder, but as in most oil mills hydraulic accumulators are provided, a similar machine is usually found with hydraulic cylinder.

Fig. 24 indicates a machine of this class arranged for the cake to be moulded upon the top of the pressing table, whilst the pressure is applied without removing the cake from the frame, thus ensuring the cake being delivered with perfectly formed edges.

In many oil mills where large numbers of presses are used, and economy in labour is a serious consideration, automatic moulding machines are provided, as illustrated by Fig. 25.

This machine is combined with the heating kettle, all the operations beyond that of placing the wrapper and tray upon the sliding carriage being done automatically by means of hydraulic power. This allows considerable acceleration in the delivery of the formed cakes; one of these machines, operated by one man, being capable of delivering as many cakes as two of the ordinary type of moulding machine; whilst the shape of the cake is retained owing to the fact that the meal is pressed whilst actually in the mould frame.

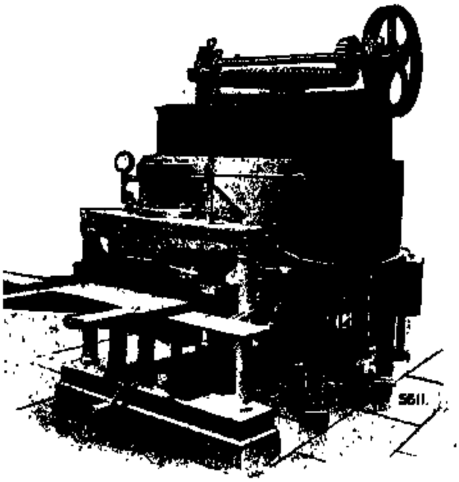

FIG. 25.—Automatic Cake Moulding Machine with Heating Kettle.
(Manlove, Alliot, Nottingham.)

Hydraulic Presses Used in Oil Expressing

Two different sorts of presses are used, viz., the **Anglo-American (plate)** and the **cage or "cylinder" (clodding)** presses. In the **Anglo-American system** (Fig. 26) the moulded seeds are wrapped in cloth bags and placed between a series of plates. The expressed oil runs down, and is collected in tanks below the press.

The plate or Anglo-American system is usually employed for the treatment of seeds requiring one pressing.

Fig. 26 shows a set of four **Anglo-American oil presses** suitable for the manufacture of oil cakes from cotton seed, linseed, and any other seeds containing not more than 35 per cent. of oil.

The formed cakes, after leaving the moulding machine, are placed between the steel press plates, which are usually corrugated and so formed to prevent the meal spreading whilst under pressure.

This type of press is also used for the second pressing of ground nuts (Arachides) or other seeds containing a high percentage of oil, which have been pressed or otherwise treated to express a certain proportion of the oil, prior to being placed in the Anglo-American presses for complete and final treatment.

In the standard press, which is constructed with a ram 16 in. diameter, the working pressure is 2 tons per square inch, giving a gross pressure of 402 tons, whilst in the second pressing press, which is used for ground nuts, etc., the ram is usually 18 or 18½ in. diameter at a working pressure of 3 tons per square inch, giving a gross pressure of 806 tons.

In the **"cage system"** (Figs. 27, 28) the seeds are confined in a closed chamber perforated with little holes, large enough to allow the oil to flow out, but small enough to retain the seed. The pressure being applied, the oil is forced out. *The advantages of the latter system are* :—

(1) Very great pressures can be applied, so that nearly all the oil is extracted at a single pressing.

(2) No exudation of the mass from the edges of the cloths or bags occurs as in the Anglo-American system.

(3) The press cakes need not be "pared."

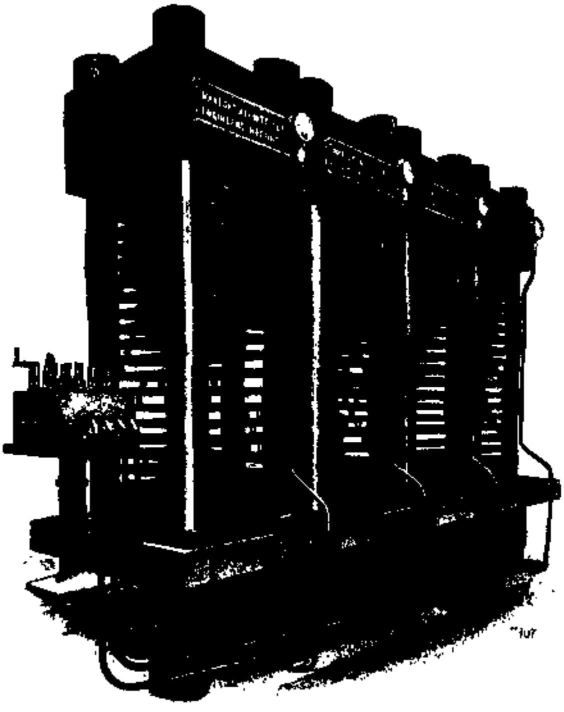

FIG. 26.—Battery of Four Anglo-American Oil Presses, having a continuous gutter for collecting the expressed oil.

(Manlove, Alliott, of Nottingham.)

Fig. 31, p. 54, shows an arrangement of two hydraulic presses on the cage press system, which are used for the purpose of expressing the maximum yield of oil at one pressing from palm kernels, copra, ground nuts, and similar seeds containing a high percentage of oil. These presses are constructed to work at high pressure, having rams 18¼ in. diameter, suitable for a working pressure of 3 tons per square inch; gross pressure, 806 tons.

The cage is constructed of a number of vertical steel bars, accurately machined and spaced at not more than $\frac{1}{100}$ in. apart, although when required these spaces can be reduced to $\frac{1}{500}$ in. apart. They are supported by a number of weldless steel rings, with a cast-steel top and bottom, the whole being accurately fitted and bolted together by three vertical bolts.

Sheet-steel oil-splashing guards are provided, all of which are indicated in Fig. 27.

The operation of working the press consists of filling the cage above referred to with meal at a high temperature, which has been previously heated and moistened in a double heating kettle, as illustrated. As the ram lowers the operator places a measure of meal in this box on the top of which a plate is placed, followed by successive layers of meal and plates, until the cage is filled. These cakes are packed by means of an upper packing ram operated by means of a foot valve and hydraulic pressure. This allows the maximum amount of cakes to be placed in the box.

Upon the completion of the filling process the loose head, which is shown withdrawn in Fig. 31, p. 54, is placed in position by means of hand-wheel, rack, and pinion, and low pressure is admitted to the main cylinder. This presses the cakes and usually causes the cage to rise on to the loose head, but if this does not happen special provision is made whereby the cage can be thus raised. Intermediate and high pressure are afterwards admitted, the whole mass of cakes being left under pressure for a varying period of time, according to the amount of oil to be obtained. The loose head acts as an upper ram, and this ensures equal pressure throughout the whole mass of cakes.

When the cakes are required to be withdrawn the pressure is released, thus allowing the cage to fall and the loose head to be withdrawn; the operation of the hand-wheel drawing the loose head automatically fixes the cage in position in order to prevent the pressure of the lower ram from raising the cage when removing the cakes.

A combination of both Anglo-American and cage systems is often employed for very oily seeds requiring two pressings, or for the production of two qualities of oil.

Self-contained Oil Mill—Cage Press System

Fig. 28 illustrates a small self-contained oil mill upon the cage press system, which is used upon estates for dealing with small quantities of copra, palm kernels, castor seed, etc.

It consists essentially of a set of rolls for the reduction of the seed to meal, a heating kettle, provided with mechanically moved stirrers, one or two cage presses, as the case may be, and hydraulic pumps for operating.

It is possible with a plant of this type to crush and press from 10-20 cwt. of seed sold. It requires not more than 9 H.P. in the smaller size and 17 H.P. in the larger size for working, whilst the percentage of oil obtained from the meal is equal to that of the most powerful mills made.

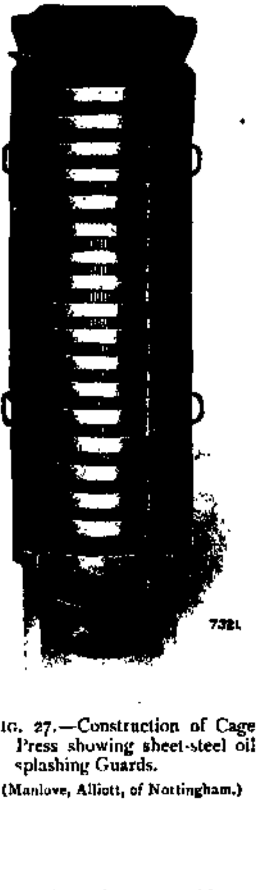

FIG. 27.—Construction of Cage Press showing sheet-steel oil splashing Guards.

(Manlove, Alliott, of Nottingham.)

Hydraulic Plant

In most oil mills it is customary to provide accumulators in order to avoid any shortage of hydraulic power, and where two or three pressures are required separate accumulators are necessary for each pressure.

Fig. 29 shows an arrangement of high and low pressure pumps in an oil mill, with accumulators in the background. The accumulators are so arranged as to automatically relieve the pump when they reach the top of stroke, and as the demands of the presses cause the accumulators to fall they restart the pumps after falling to a predetermined position.

Cake Paring Machine

Fig. 30 illustrates a cake paring machine for the removal of the oily edges from the cakes made in the Anglo-American presses. These cakes being held in wrappers and between open plates, it naturally follows that the oil is expressed very thoroughly from the centre portion of the cake, but the edges usually contain considerably more oil than it is to the advantage of the seed-crusher to allow to leave the factory, and for this purpose the edges of the cake are usually removed by the machine illustrated, re-ground, and re-pressed.

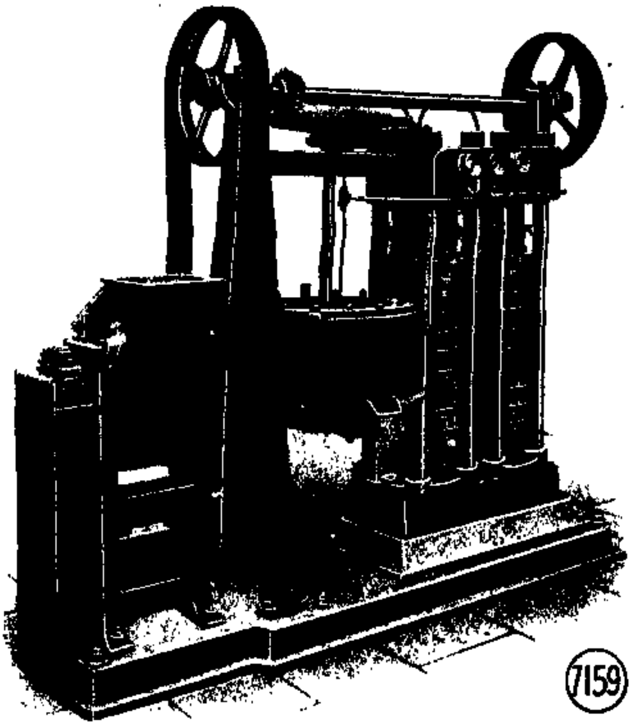

Fig. 28.—Self-contained Oil Mill, Compressing Rolls, Heating Kettle for Meal, and two "Cage" Presses.

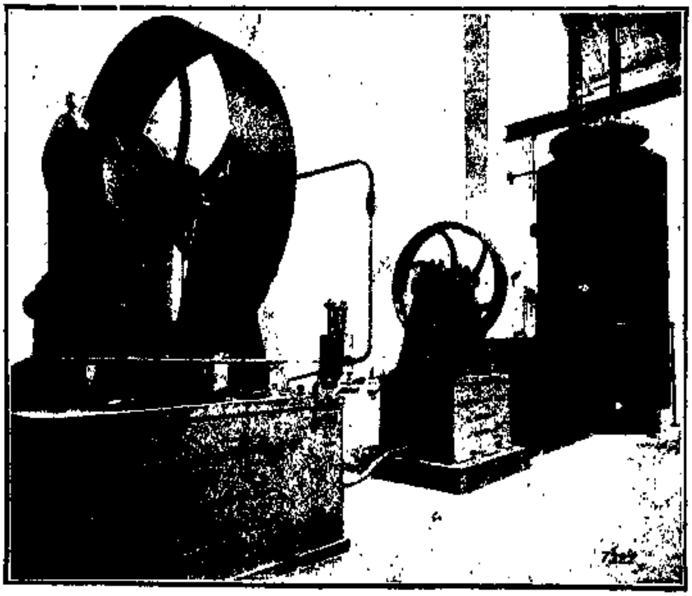

Fig. 29.—Hydraulic Pumps for Oil Presses, with Accumulator.

The machine consists of a table upon which the cake is placed, with guide bars; the internal drive with cutter knives arranged to form also a worm conveyor, and the travelling knife operated by means of a crank. The travelling knife removes the edges of the cake, which are there partially broken, and conveyed by means of the worm usually to an elevator, which delivers them to either rolls or stones for further reduction before re-pressing.

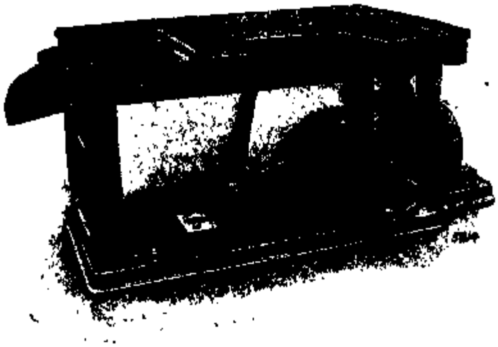

FIG. 30.—Cake Paring Machine.
(Manlove, Alliott.)

Summary.—A complete scheme of operations involved in oil pressing is indicated in Fig. 32, which the reader should consult.

CHAPTER VI

Manufacture of Vegetable Oils by Pressing

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MANUFACTURE OF VEGETABLE OILS BY PRESSING

Treatment of Individual Seeds

DIFFERENT seeds require a somewhat different treatment; linseed and cotton seed, for example, require one crushing, while castor seed and copra (the flesh of the coco-nut) are usually crushed twice. We will outline the process usually employed in the case of the more important seeds.

Linseed.—The seed must be perfectly clean. It was formerly always necessary to pass it through a screening machine to remove impurities; but now much of the linseed on the market is sold on the basis of 95 per cent. purity, and some at 97 per cent.; such seed is ready for immediate use without further cleaning. The clean seed is now passed to the rolls or crushing machinery C (Fig. 32, which represents a complete oil mill designed by Rose, Downs, & Thompson, of Hull). The seed is passed into the hopper in the usual manner, and is distributed to the crushing rolls (made of hardened chilled iron) by a fluted feed roller of the same length as the crushing rolls placed at the bottom of the hopper. The feed of the seed to the rolls can be altered at pleasure. As the seed passes the feed roll, it falls on to a guide plate that carries it between the first and second rolls. After passing between these and being partially crushed, the seed falls on to a guide plate on the other side, and is carried between the second and third rolls, where it is further crushed. It then falls on another guide plate, which carries it between the third and fourth rolls, where it is ground still more. In large rolls it can be carried between a fourth and fifth roll before it receives the final crushing.

The crushed seed or meal is now raised by the elevator D (Fig. 32) into the kettle or heater F, where the mass is warmed by steam to the right temperature in order to facilitate the flow of oil when in the press, the heat also serving to coagulate albuminous matter in the grain. From the kettle the heated grain falls into the moulding machine or former G, where it is squeezed into cakes suitable for placing in the hydraulic press. The moulding machine also serves to accurately measure the amount of crushed or heated meal required for a cake, thus ensuring the production of cakes with little variation in weight.

The cakes thus formed are wrapped in cloth bags and placed in the hydraulic press (Fig. 32, H, and Fig. 26). One of the larger Anglo-American presses will take some sixteen cakes, 28 in. by 12 in. each, separated from each other by a steel plate. When the press is full the pressure is slowly turned on, and the oil begins to flow from the compressed meal, at first slowly and then very rapidly, the oil running down the sides of the machine into a tank in which the presses stand, and from which it is forced by a pump to the filters or store tanks. When the pressure has been applied for three or four minutes the flow of oil practically ceases, the oil simply dripping from the compressed cakes until the pressure is released. If more presses than one are being used, they are filled one after the other until the whole battery of presses is charged. The meal cakes are allowed to remain under pressure from ten to forty minutes (the exact time varying with the special conditions), and then the pressure is released on the first press in the series and the ram allowed to descend. The cakes are removed one by one as the ram descends, and fresh charges of meal introduced wherever a cake is removed. The cakes, as they are removed, are placed on the paring machine, their cloth bags stripped off, and their oily edges cut away by the paring machine, these oily parings being reduced to meal again by small edge-stones J (Fig. 32), and returned to the kettle F (Fig. 32) to be worked up again. If a cage or circular box (clodding) press is employed the cake need not be pared—one great advantage of the latter system. The finished cakes are placed on racks in which they are allowed to stand until perfectly cool, when they are removed to the cake house or store. The cake racks are usually placed in the most draughty part of the mill to assist the cooling process. Other similar small seeds are treated in much the same manner as linseed. Among these we may mention sunflower, mustard, China or soya beans, some kinds of rape seed, poppy seed, and similar seeds requiring but a single pressing.

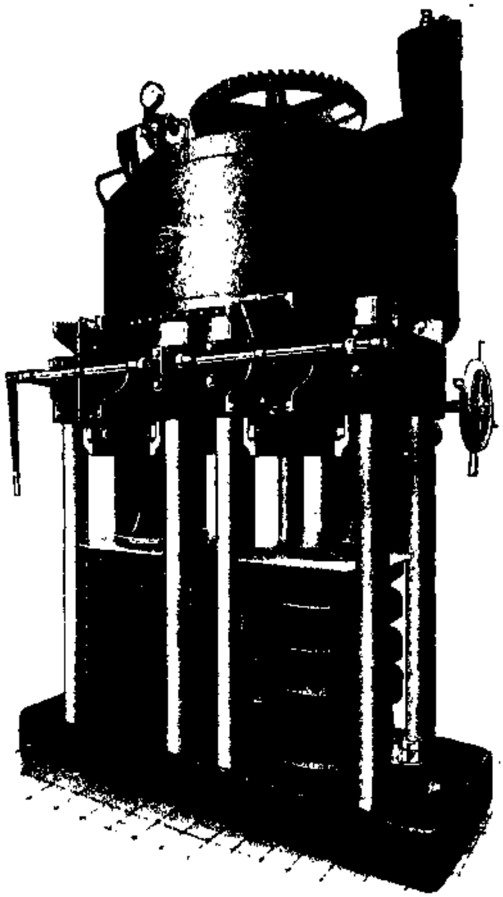


FIG. 31.—Cage or Circular Box (Clodding) Oil Press.
(Rose, Downs, & Thompson, Hull.)

FIG. 32.—A COMPLETE ANGLO-AMERICAN OIL MILL.

(Designed by Rose, Downs, & Thompson, of Hull, England.)

In the above illustration the complete process is shown. The seed passes through the rolls C; from these an elevator D places it in the kettle F, from which it passes into the moulding machine G, where it is measured, formed, and compressed; and thence it passes to the presses H. The cakes, after being pressed, are cut to size in the paring machine I, and the parings reduced to meal by the small edge-stones J. The parings are returned, to be reworked, to the kettle F.

The presses H stand in a tank into which the expressed oil falls, from whence it is forced to the store-tanks, or filters, by a pump.

[*To face page* 54.

Linseed usually contains 38-40 per cent. of oil, and the press cake 6-10 per cent. The following figures are instructive :—

One ton of linseed containing 40 per cent. of oil yielded—			
750 lbs. oil, value at £57 per ton	£19	1	10
1,490 ,, cake, value at £20 per ton	13	6	0
	£32	7	10
Cake, 10 per cent. oil :—			
149 lbs. oil, value at £57 per ton	£3	15	11
1,341 ,, dry residue, value at £15. 10s. per ton	9	5	7
	£13	1	6

(For properties of linseed oil see p. 133.)

Cotton Seed also requires but a single pressing. Two varieties exist—the black seed and the white; the former has its husk quite clean and free from adherent cotton (example, Egyptian cotton seed), while the husk of the latter is covered with short white cotton fibres (examples, American cotton seed, Indian cotton seed). Both classes of seed are treated in England in much the same way as linseed, the only difference being that the seeds as they leave the rolls are ground beneath powerful edge-stones before passing on to the kettles. In the United States, however, the cotton seed is first decorticated, *i.e.*, the husk of the seed is entirely removed, only the resulting kernels or "meats" being pressed. The advantage of this treatment becomes obvious when it is realised that practically 50 per cent. of the seed is husk, and that consequently a mill removing this by using decorticators can treat twice as much seed as a mill of the same size, but without decorticators. The husks are used as cattle food, fuel, or manure, as the case may be.

Cotton seeds on the average consist of 60 per cent. kernels and 40 per cent. husk. They contain 18-24 per cent. of oil, which is contained in the kernels.

The American kernels are smaller than the Egyptian.

Delinting Cotton Seed.—In England the seed is usually reduced between rolls and pressed. In the case of American seed, however, it sometimes pays to remove the lint from the seed, as the excess lint can be sold as cotton, and an excessive amount of lint may lower the value of the cotton-seed cake resulting from the pressing.

The delinting machines consist of a box, the bottom of which is a grating. Through this grating project the tips of a large number of fine-toothed circular saws placed on a cylinder run at 350-400 revs. per minute. The seed in the seed-box is churned up by the saws, the teeth of the saws catching in the lint and pulling it away from the seeds. The delinted seed escapes down a shoot, while the lint adhering to the saws is picked off the teeth by a circular brush revolving at 1,300-1,500 revs. per minute.

An air current is directed on to this brush by a fan, and this blows away the lint from the brush into a revolving cylindrical cage of wire cloth, on which the lint collects in layers and is removed from time to time.

To prevent the teeth of the saw being damaged by iron nails, etc., which are found in the seed, the seed is made to traverse a series of electro-magnets before passing on to the saws.

About 20 lbs. of lint are obtained per ton of seed treated, and a machine dealing with 3-20 tons of seed per twenty-four hours will absorb 3-10 H.P.

Decorticating Cotton Seed.—The cotton-seed oil is produced from the kernels, and these are surrounded by husks, which contain strong deep brown colouring matter and little or no oil. There is thus a considerable advantage in removing the cortex or husks of the seed before crushing, and thus pressing the kernels alone. The advantages are—(1) The oil is of a better colour, (2) the press cake is of a better quality, (3) the material treated being far richer in oil than the whole seed, a greater amount of oil can be obtained in a given time from a press of a given size.

This is obvious from the consideration that the seeds on the average consist of 60 per cent. kernel and 40 per cent. husk, and the 18-24 per cent. of oil is concentrated in the kernels alone. Consequently 100 tons of whole seed have to be put through the mill to yield 18-24 tons of oil, against 60 tons of kernels.

The disadvantage is the capital expense of the extra machinery required.

The **decorticating machine** put on the market by Messrs Rose, Downs, & Thompson, Ltd., of Hull, consists of a rotating barrel carrying ten knives crosswise on its periphery; opposite this is a fixed "breast" carrying three stationary knives, also placed crosswise. The knife barrel runs at 1,500 revs. per minute.

The seed is fed in at a hopper and falls on the rotating barrel, and is caught between the rotating and fixed knives, and the husk is removed. The husks and kernels together are carried round to the lower edge of the "breast," and are collected and separated automatically. A machine dealing with 10 cwt. of seeds per hour absorbs 6 H.P. for driving.

The **separated husks** are used as a cattle food, also as fuel under the boiler, and sometimes as a manure.

Crushing the Seed.—The seeds are reduced in rolls similar to those used for linseed.

Pressing the Seed.—The seeds are next pressed, a single pressing being usually sufficient. (For properties of the oil see p. 131.)

The cotton-seed meal (*i.e.*, the press cake ground up) is best used as a cattle food, but is sometimes used as a manure for cotton, tobacco, sugar cane, etc.

The following figures are instructive :—

1 ton of undecorticated Egyptian cotton seed containing 24 per cent. of oil was crushed and then yielded :—

340 lbs. oil, value at £53 per ton	£8 4 11
1,892 ,, cake, value at £15. 10s. per ton	13 1 9
	£21 6 8
Cake, 10 per cent. oil :—	
189 lbs. oil, value at £53 per ton	£4 9 4
1,703 ,, dry residue, value at £11. 7s. per ton	8 12 5
	£13 1 9

Castor Oil

The castor tree or shrub grows in all tropical and sub-tropical lands, especially the East Indies. The fruit consists of a rough outer shell or pod, enclosing a white soft kernel covered by a husk, underneath which is a thin brittle shell. The kernel carrying the oil is thus enclosed between two outer casings.

The kernel yields 46-53 per cent. of its weight of oil and forms 80 per cent. of the seed.

Preparatory Treatment of Castor Seed.—The seed is first shelled in a special machine (supplied by Rose, Downs, & Thompson, Ltd., of Hull).

The seeds are fed into a hopper, and are thence carried by a rotating worm between a pair of discs. The pods are rubbed between the discs, and their outer casings are broken. The mass falls into a hopper, and is then subjected to an air blast from a fan, which blows away most of the husk into a collecting chamber. The heavier beans, with some adhering husk, pass on through a pair of rolls on to a shaking separator. The material next encounters a blast of air which removes the last portions of the pod, the heavier beans passing on into a hopper. A machine dealing with 10-20 cwt. per hour absorbs 6-8 H.P.

Decorticating Castor Seed.—The preceding machine removes the outer husk. The inner shell may now be removed in a special machine.

Rose, Downs, & Thompson, of Hull, market a machine in which the beans fall from a hopper between a pair of cylindrical rolls, the space between which is carefully adjusted.

The beans passing between the rolls are cracked, and the broken shells and kernels fall on to a shaking separator. Here they fall from tray to tray, and encounter in so doing a blast of air. The lighter shells are thus separated and issue through one passage, while the cracked beans pass out through another.

A machine dealing with 20 cwt. of beans per hour requires 7 H.P. to drive it. The crushing rolls make 100 revs. per minute, the shaking separator shaft 500, the fan 1,000, and the feed roll 100.

It may be noted that it is essential to free the castor-seed kernel from its second or inner covering if a good clear quality of **hot-drawn** oil is aimed at. For most purposes, however, the oil obtained by pressing the beans with only the outer pod removed is good enough.

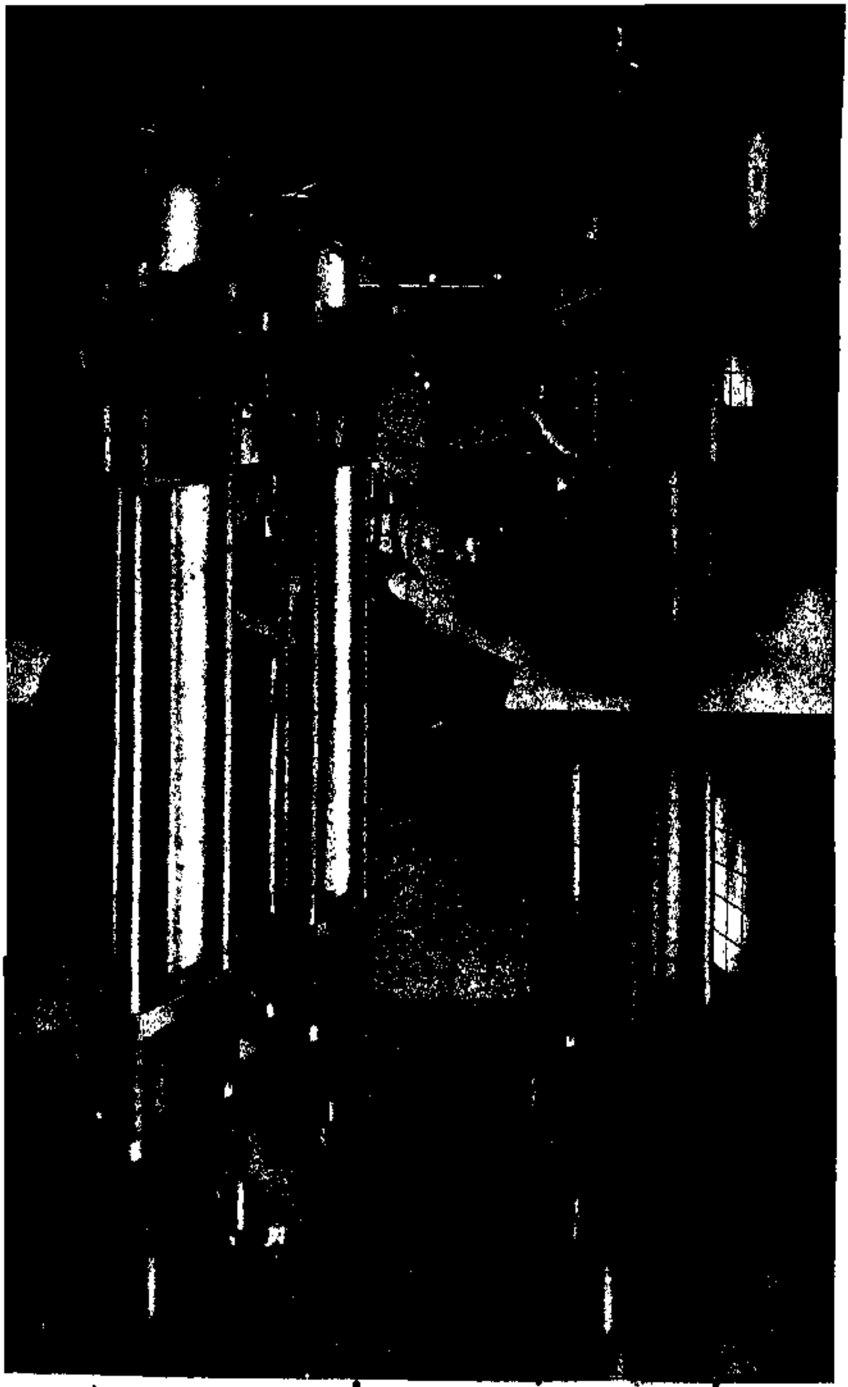


FIG. 33.—IMMENSE CAGE PRESSES USED FOR EXPRESSING CASTOR OIL FROM CASTOR SEED.

(Rose, Downs, & Thompson, Ltd., Hull.)

[*To face page* 57.

Pressing Castor Seed.—This seed, being very rich in oil, is usually worked twice, the first time cold and the second time hot. The seed must be very well cleaned before pressing, which operation is best carried out in cage presses, the seed being pressed in its natural state without any preliminary crushing at all. The best medical oil is the cold-drawn, and consequently it is greatly to the advantage of oil manufacturers to press out as much oil as possible at a single pressing. Immense presses have been erected for this purpose in some mills. A set of four giant presses is shown in the plate (Fig. 33), which represents a modern and improved type of press battery, designed by Rose, Downs, & Thompson, and used in some large English oil mills. Each set comprises two presses, having cages or cake chambers 19 in. diameter and 9 ft. long internally. These chambers are finely perforated, so that while retaining the solid residue, they allow the oil and other fluids to escape. Each press has its own kettle, 60 in. by 26 in., while the rams are forced at a pressure of 3 tons on the square inch. The seed is fed whole to the kettles, are there heated by steam to about 32° C., and afterwards pressed at 3 tons on the square inch. The resulting cakes contain from 8.5-10 per cent. of oil. The whole battery of four presses is worked by two men, and press a total weight of 2 tons of seed per hour.

Presses of this type are specially suitable for the first pressing of all kinds of very oily seeds, such as castor, sesame, ground nuts, copra, palm kernels, etc., producing a maximum quantity of first pressing oil, and reducing the oil in the cakes to such small proportions as to render a second pressing unnecessary, or permitting the remaining available oil to be extracted by solvents. In view of the high prices commanded by first-pressure oil, such presses effect a very great economy, although the first cost is high. In mills where less powerful presses are employed, the solid cakes resulting from the first pressing are ground up in suitable machinery, warmed, and pressed again.

A very effective modern process is to first press with a cage machine, and then extract the bulk of the oil from the resulting cake by solvents. Such extracted oil cannot be used for edible purposes, but is valuable for soap-making, lubricating, etc. The meal from the solvent contains only 1 per cent. of oil. This mixed process is largely worked on the Continent.

The medicinal use of castor oil depends upon the presence of an alkaloid, which in excess is poisonous. This alkaloid is retained in considerable quantities in the residue left after pressing the seeds, and consequently castor-oil cake is unfit for cattle food. It is best extracted with solvents to recover all the oil possible, and the residue used as a fertiliser.

Olive Oil

The olive tree is chiefly cultivated in the countries bordering the Mediterranean. All parts contain the oil. The fruit consists of rind, flesh, stone, and seed kernel. 40-60 per cent. of the oil is contained in the fleshy part, and is the best oil for edible purposes. The fruit is gathered before it is quite ripe, and is then peeled and stoned. The flesh is pressed by itself and yields the best oil. The kernels are pressed separately and yield an inferior "olive-kernel oil."

The fleshy pulp left after the pressing may contain 20 per cent. of oil. It is ground up with hot water, allowed to stand, and the broken-up cellular tissue which rises to the surface is then pressed again for a second quality oil.

The residue is often extracted with carbon disulphide, the extracted oil being of a deep green colour owing to dissolved chlorophyll from the fruit. This oil is sold to soap-makers.

Many works do not stone the fruit first, but crush the olive as a whole, thereby obtaining a better yield of an inferior oil, since the poorer oil from the stones now mixes with the oil from the fleshy part. (For properties of the oil see p. 130.)

The first pressed oil is always sold as an edible oil. The second or third pressings go for burning, soap-making, or lubricating purposes. The press cake is sold as a cattle food, while the residue left after the carbon disulphide extraction is sold as a fertiliser.

Palm Oil and Palm-Kernel Oil

These oils are of great and growing importance.

In 1908 the United Kingdom imported palm oil to the value of £2,300,000. Germany in the same year imported palm kernels to the value of £3,300,000, the United Kingdom and other countries taking as well £1,900,000 worth.

Owing to the outbreak of the European war great changes occurred.

In 1914 the United Kingdom imported £1,400,000 of palm kernels, and in 1915, £2,500,000.

The fruit of the African oil palm is on the average 1¼ in. long and ¾ in. maximum width, and grows in large bunches weighing about 14½ lbs., and measuring 12 in. long by 10 in. across on the average. The fruit consists of a fleshy outer layer or pericarp surrounding a hard shell, inside of which is the seed kernel. The fleshy **pericarp** forms about 35 per cent. of the whole, the **shell** 50 per cent., and the **kernel** 15 per cent. The pericarp contains 50 per cent. of oil, while the kernels contain 45 per cent.

Palm oil is derived from the **fleshy pericarp,** while **palm-kernel oil** is derived from the kernel inside the shell. (For properties of the oil see p. 129.)

The fruit rapidly deteriorates soon after gathering, so that it is impracticable to ship the whole fruit to Europe for oil extraction. Consequently the **palm oil** is recovered by the African natives on the spot from the fleshy pericarp, while the nuts or kernels are sent overseas to be crushed in European or American factories, the resulting product being "**palm-kernel oil.**" It must be particularly noted that **palm oil** from the pericarp is quite a different product from **palm-kernel oil** from the nuts.

Working up the Fruits for Palm Oil.—(*a*) *Native Method.*—The native method is crude, and results in the loss of 50-70 per cent. of oil, the oil which is obtained being also largely hydrolised to fatty acids. The ripe fruit is allowed to ferment or rot in the presence of water, so that the hard fleshy pericarp is softened and so can easily be separated from the nuts, which is done by beating the softened fruit to a pulp, and then picking out the nuts from the mass by hand. The pulp is then boiled with water, and the oil skimmed off the surface.

Once hydrolysis of the oil sets in it continues, so that frequently palm oil will arrive in Europe containing 50 per cent. of free fatty acid. Consequently, palm oil is usually only fit for making soap and candles. It has been suggested to extract palm oil on the spot, and place immediately in carefully sealed drums quite air tight so as to stop progressive hydrolysis during shipment.

(*b*) *Modern Method.*—Many attempts have been made to improve on this treatment. For example, if the perfectly fresh (and not rotting) fruit is treated it yields an oil not containing more than 8 or 9 per cent. of fatty acids, against 40-50 per cent. fatty acids obtained in oil from bruised fruits.

The best method of preparing palm oil is to steam the fresh fruit for two or three hours, afterwards removing the pericarp and treating the whole mass in a centrifugal extractor, the resulting oil being of the first quality. The pericarp is then separated from the nuts and treated with steam, afterwards being treated in a hydraulic cage press, as previously described. This ensures the highest possible yield of oil of a slightly inferior quality.

Many attempts have been made to do without treating the fruit with water or steam, as this is stated to partially decompose the oil into fatty acids.

Messrs A. F. Craig, of Paisley, have placed machines on the market whereby the fruit is passed whole and dry between two horizontal curved plates rotating rapidly in opposite directions, and fitted with closely curved blades. The outer fleshy part of the fruit—the pericarp—is thus cut away from the interior nut and thrown away from the stones by the centrifugal force of the rotating plates. The stones left are then passed through another machine, where wire brushes scrape off from them any remaining fragments of the fleshy pericarp.

The stones are thus completely separated from the pericarp, and each mass is then pressed separately for oil in the usual way.

Messrs Lever Bros. erected a modern factory for dealing with the fruit on modern lines on the spot on the West Coast of Africa. The scheme, however, failed on account of native opposition to bringing in fruit to the factory, coupled with tribal and other jealousies, and the disinclination of the native to work for money or goods for which he has no use or desire.

Treating Nuts for Palm-Kernel Oil.—The stones are usually shipped to Europe to the oil mills and then passed through cleansing machines to separate sand, dirt, iron fragments, etc. Next the nuts pass to shredding and reducing rolls, whereby they are converted into a meal. The meal is then pressed in the ordinary way in hydraulic presses, and the fresh oil is, after refining, much used in the margarine trade.

The palm-kernel oil cake is used as a cattle food. Being somewhat deficient in nitrogen, it is best used in the form of a composite meal, mixed with other ingredients. It is sometimes sold as a fertiliser.

Very often the crushed meal is extracted with solvents. A greater yield of oil is thus obtained, but the residues have less value as a cattle food.

Attempts have been made to deal with the nuts separated on the spot in Africa. They are passed through machines for cracking the nuts, the shells being then separated from the kernels by automatic shaking or other devices. The kernels are then crushed in presses for the oil in the usual way. Messrs Craig of Paisley's **nut cracker** and **separator** is composed of a rapidly rotating drum placed inside a casing. The nuts fall into the drum and are thrown with great force against the outer casing, and so are cracked. The cracked shells and kernels are then fed down a shaking separator (in the form of an inclined plane, provided with a special surface and a shaking motion). The kernels pass to one end of the tray and the shell fragments to the other. The shell fragments can be used as fuel.

The **technical advantages** of extracting the palm and palm-kernel oil in Africa on the spot are at first sight very great.

For example, the fresh fruit is gathered locally and brought into the factory. Before any deterioration of the fruit can set in it is passed through machines for removing the flesh or pericarp from the fruit as previously described, and the separated flesh treated for palm oil immediately. The nuts are separated and stored, and then worked up later in the factory when the season for the palm has passed. So that the factory is thus theoretically capable of working continuously all the year round, and not only at the season when the palm fruits are ripe, and so the staff can be kept together.

An equipment of such a mill would consist of: (1) Preliminary screens for removing sand and other materials which the natives sometimes mix with the fruit; (2) depericarping machines for removing the flesh from the nuts; (3) brushing machines for cleaning the nuts from fragments of pericarp; (4) nut-cracking and kernel-separating machines; (5) reducing mills for the kernels; (6) shredding rolls for the kernels; (7) heating kettles; (8) bar cage crushing presses, consisting of a preliminary press, and intermediate press, and a finishing press.

Designs of such a factory have been prepared by Messrs Craig, of Paisley.

The **technical disadvantages** are very serious of working the palm fruits completely on the spot, and in the case of Lever Bros. led to the abandonment of such a factory.

These difficulties are: (1) Native opposition; (2) inefficient and unskilled labour on the spot; (3) loss of the oil cake and residues. If exported, freight would have to be paid on these, and in Europe a good profit is made by selling the residues from the oil mills in the highly industrial countries to dairy farmers and others who supply these industrial populations with milk and food.

In Europe the labour is highly intelligent and efficient, and an immediate market is met for almost every product from the oil mill. Consequently most firms still prefer to import from Africa the raw products, and work up the nuts in Europe.

The industry, however, is only in its infancy, and is capable of great development.

Coco-Nut Oil

This very important oil is obtained by pressing "**copra**"—which is the flesh of the coco-nut—the fruit of a tree of the palm family. (For properties of the oil see p. 129.)

The tree from which cocoa is derived is of an entirely different nature, and coco-nut oil must not be confused with cocoa-butter, which is obtained from the coco bean.

The coco-nuts are gathered by the natives and brought to depots. The nuts are then split open and placed to dry.

The **splitting** is usually performed by means of a hammer, but recently it has been performed by machinery. Messrs Rose, Downs, & Thompson, Ltd., of Hull, have placed on the market a machine dealing with 2,000 nuts per hour, requiring about 2 H.P. to work it. The nuts are fed into the hopper of the machine with their husks on, and, running down three bent plates or knees which act as guides, come into contact with three circular knives of 17 in. diameter, provided with saw-like teeth, the knives being placed at 120° apart, and making 25 revs. per minute.

The nuts are cut into three parts, and the parts are carried forward and fall on the base of the machine. The **drying** of the nuts is usually carried out by placing them in the sun. Kilns of rude construction are also employed, but modern practice favours the erection of a lightly built galvanised iron house, beneath the floor of which steam heating pipes are placed.

The drying must be carried out carefully, because if too rapid the flesh is discoloured and the oil is difficult to refine, while if too slow the oil hydrolises, with the production of free fatty acids.

The final result of the drying process is that the flesh becomes loosened from the shell and loses about 50 per cent. of its weight.

The dried **copra** is exported to Europe in lumps, and then goes through the following processes in order to reduce it to a meal before pressing.

1. The copra is sent over a **magnetic separator** in order to remove from it fragments of iron, nails, hammer heads, iron nuts, etc., which it occasionally contains, and which, if allowed to get into the machinery, may cause a serious breakdown.

The apparatus consists of a sloping, shaking tray (often made in the form of a screen to eliminate sand, etc.), at the end of which is a power-driven magnetic barrel provided with seven rows of magnetic studs, each row being mounted on a separate commutator section of the barrel.

The non magnetic copra passes over the rotating barrel and falls into a suitable hopper below; the iron fragments, however, adhere to the magnetic studs and are carried round the rotating barrel to the back until they reach a position whereat the section of the barrel to which they are adhering is automatically demagnetised for a moment so as to allow them to drop off on to a tray below.

Such a machine, dealing with 1-1½ tons per hour, requires 1 H.P. to drive it. The magnetising current is usually 7 amperes at 40 volts.

2. The copra is now reduced to a meal in three, four, or five separate stages.

The copra lumps are usually first run through a **preliminary breaking machine**.

The preliminary breaker of Manlove, Alliott & Co., of Nottingham, consists of a cast-iron barrel, ribbed internally to prevent the copra rotating as a mass within it. Inside this casing runs a power-driven segmental worm having a coarse pitch at the feed end and a finer pitch at the delivery end. The copra fragments are by this means driven down the barrel and forced through a hardened perforated steel plate at the end. A four-bladed knife revolves against the worm side of the plate and cuts the copra as it passes through the perforations, also assisting its passage through these holes. Sometimes an **ordinary disintegrator** is used for smashing up the copra.

The partially broken copra is now reduced to a finer state of division by means of a series of rolls which shred and crush it.

In the first sets of rolls the rollers are of chilled cast iron, and rotate at different rates, so that the action is a **shredding** and **grinding one**.

Fig. 18 shows a stack of three pairs of chilled cast-iron rolls used for this purpose, the upper rolls are usually fluted, while the lower rolls are plain. The rolls are often 15 in. in diameter and 36 in. long, and deal with 12-20 cwt. of copra per hour, and consume 8-12 H.P., the rolls making 45-50 revs. per minute.

The **final reduction** to a fine meal takes place in a stack of five rolls rotating at equal speeds, the action required being one of **rolling**, not of **grinding** (Fig. 21)

The uppermost rolls are usually lightly fluted, while the final rolls are plain. The output of the rolls is 10-20 cwt. per hour.

3. The fine copra meal thus obtained is now **pressed for oil**.

The meal from the last set of rolls is automatically conveyed to the kettle or heater of the presses, which may be either "Anglo-American" or "cage" type, for the first pressing. Usually the material is worked cold the first time, the resulting cakes being ground up and heated for a final pressing. This process, with slight deviations, is used for treating all very oily seeds, such as ground nuts (Arachides), palm kernels, sesame, copra, etc.

Soya-Bean Oil

The soya bean is imported from China, Manchuria, and Japan. The oil in Europe is now as important as cotton-seed oil, while the press cake forms a most important food for milch cows, being as valuable as linseed or cotton-seed oil.

Soya beans contain 18 per cent. oil. In the press they yield 10-13 per cent. (For properties of the oil see p. 132.)

Rape or Colza Oil

The rape plant is grown largely in Europe, Russia, and especially in British India.

The seed contains 33-43 per cent. of oil, and is frequently extracted by solvents. (For properties of the oil see p. 131.)

It is stated that the oil contains a poisonous principle, and in consequence rape seed cake is not valued as a cattle food. It is usually used as a manure.

Mustard Oil

Mustard oil is obtained from the black, white, or wild mustard plant. It is very similar to rape oil. The cake, after crushing, yields the ordinary domestic mustard. (For properties of the oil see p. 132.)

Sunflower Oil

The sunflower is cultivated on a very large scale in China, Russia, India, and Italy. The oil obtained from the seeds is considered to equal olive oil for edible purposes.

The seeds contain 20-23 per cent. of oil. (For properties of the oil see p. 132.)

The **press cake** is rich in nitrogenous matter, and forms a very valuable and palatable cattle food. The seeds, indeed, are used in Russia for human food.

Poppy-Seed Oil

Poppy seed contains 45-50 per cent. of oil. The seeds are usually pressed twice. The first pressing is carried out in the cold, and the "cold-drawn" oil thus obtained is almost colourless and odourless, and possesses a pleasant taste. It consequently forms a valuable salad oil and artists' oil.

The second pressing is carried out hot, and yields an inferior oil.

The press cake is rich in nitrogen, and forms a valuable cattle food. (For properties of the oil see p. 132.)

CHAPTER VII

Manufacture of Vegetable Oils by Extraction with Solvents

CHAPTER VII

MANUFACTURE OF VEGETABLE OILS BY EXTRACTION WITH SOLVENTS

EXTRACTION OF OILS AND FATS BY MEANS OF VOLATILE SOLVENTS.

THE oil cakes obtained by the pressing process may contain anything between 7 and 10 per cent. of oil. Such cakes are often sold as a valuable cattle food. Occasionally, however, when larger quantities of oils and fats than can be obtained by pressing are desired, the rest of the oil is extracted by solvents, which can be easily made to remove all except, perhaps, 1 per cent. Bones are extracted in the same manner.

Industrial Solvents.—On the large scale four solvents are employed, viz., carbon disulphide, petroleum ether (benzine), carbon tetrachloride, and benzene (benzol).

Chloroform and **ether**, although excellent solvents, are at present too dear to employ for extracting on the large scale.

Carbon disulphide, CS_2, boils at 46° C., and has a sp. gr. of 1.293, sp. ht. 0.16, latent heat of evap. 79.9. It is a colourless liquid and smells something like chloroform. When impure, however, it contains evil-smelling sulphur compounds, from which it may be purified by distilling first over sodium carbonate and then over freshly pressed plant oils, which retain these impurities almost completely. Carbon disulphide easily inflames, and so is a dangerous substance. Its vapour sometimes catches fire when in contact with hot metallic surfaces heated to about 150° C., so that a violent explosion can be caused merely by a hot steam pipe or bearing heated by friction.

Extraction with carbon disulphide has reached a very high degree of safety and perfection in France.

The carbon disulphide is heavier than water, and is kept safe from all danger of inflammation by being covered by a layer of water during the whole time it is in operation.

Pure carbon disulphide has no action on iron. Impure carbon disulphide is said to attack iron, and is said to have caused ignition owing to this action.

The vapour of carbon disulphide is poisonous. A technical disadvantage is its higher specific gravity.

With **petroleum ether**, boiling between 80°-120° C., the danger of inflammation is much less and at the same time it is cheaper. It is, therefore, gradually replacing carbon disulphide. Carbon disulphide, however, is the better solvent, resinous fats and old palm oil being much more soluble in it than in petroleum. Sp. gr. 0.72-0.75, sp. ht. 0.5, latent heat of evap. 80.

The great advantages of **petroleum ether (benzine)** are—(1) it is entirely without action on metals; (2) its low specific gravity.

It should, therefore, be very carefully distilled, so that strong-smelling, high-boiling oils are entirely removed from it before use. The fraction 90°-110° C. is the best to use for solvent extraction, but 100°-125° C. fractions are mostly used at the present time.

Carbon tetrachloride, CCl_4, is a good solvent, being easily volatile (B.P. 76.5° C., sp. gr. 1.62) and non-inflammable (sp. ht. 0.21, latent heat of evap. 46.4). It is being employed for extracting bones and fats, the products obtained having a good colour; the odour of the tetrachloride can be completely expelled by blowing steam through the oil. Oils extracted by petroleum spirit always retain its smell. The main disadvantage that carbon tetrachloride suffers from is its great weight (sp. gr. 1.582), its dearness, and the fact that it attacks iron and copper work in the presence of moisture, and hence lead-lined vessels must be employed. It must be noted that both carbon disulphide and carbon tetrachloride exert a poisonous physiological action, whereas petroleum spirit is not poisonous enough to affect the workmen.

Other chlorhydrocarbons have been placed on the market for extracting purposes. **Trichlorethylene,** C_2HCl_3, boils at 88° C., has sp. gr. 1.47, sp. ht. 0.22. Attacks iron and aluminium, and is best used with lead-lined vessels. The same applies to **perchlorethylene,** C_2Cl_4, B.P. 121, sp. gr. 1.62, sp. ht. 0.22; also **tetrachlorethane,** $C_2H_2Cl_4$, B.P. 147° C., sp. gr. 1.60, sp. ht. 0.27; also to **pentachlorethane,** C_2HCl_5, B.P. 159, sp. gr. 1.70, sp. ht. 0.27.

All these chlorhydrocarbons hydrolise to a certain extent when water is present, forming hydrochloric acid, which attacks iron and copper and aluminium, but not lead, to a great extent, and also causes discoloration of the fats.

Trichlorethylene, however, has been used recently on the large scale in iron extractors for recovering fats where absolute whiteness is not important.

The great advantage of all these **chlorhydrocarbons** is their non-inflammability.

Benzol (benzene) boils at 80.5° C., and freezes at 0° C. Its specific gravity is 0.8799 at 20° C. The substance is an excellent solvent for fats, but is not so widely used as benzine or petroleum ether. It is very difficult to eliminate from oil and meal.

General Remarks on Solvents

The suitability of a solvent for industrial uses is influenced by the following considerations:—

(1) **Cheapness.**—In all extraction plants the solvent is recovered by evaporation and condensing the vapours. A small amount of solvent, however, is invariably lost on every extraction, being in part retained in the oil or seed, and in part due to leakage of vapour through joints, and in part to imperfect condensation. Hence the cost of a solvent is of prime importance, and for this reason many excellent solvents have failed to establish themselves on the large scale, although considerably superior in many of their properties to those now in common use.

If a plant could be designed in which there was practically no loss of solvent the first cost of solvent would be almost immaterial, as the expense would be an initial one, and a given quantity would suffice for any number of extractions.

(2) **The Solvent should not Act on Metals.**—Since iron is the cheapest metal to use, a solvent which does not act on iron has technically a great advantage.

Copper, aluminium, and lead-lined vessels are employed very extensively, but of course are expensive. The depreciation of plant is of considerable financial importance.

(3) **Non-inflammability.**—Solvents which are non-inflammable are technically very desirable, since the cost of fire insurance is thereby much diminished. The danger of explosion and fire are, however, in modern plants very small.

(4) **A low specific gravity** is an advantage, because since a given **volume** of solvent is essential for extraction of a charge of seed or bones, it is obvious that a solvent of high specific gravity is dearer than one of lower gravity. To give a concrete case, 1 ton of petroleum ether (benzine) of sp. gr. 0.72, occupies 301 gallons, whereas 1 ton of carbon tetrachloride of sp. gr. 1.632 occupies 137 gallons. Hence 1 ton of petroleum ether will go $301/137 = 2.2$ times as far as 1 ton of carbon tetrachloride. Hence, in order to get the **comparative prices** of a number of solvents, we should multiply their **price per ton** by their **specific gravity.**

There is one advantage appertaining to solvents of higher specific gravity than water, and that is they can always be kept covered with a layer of water, so as to stop loss by evaporation and also diminish any danger of fire if they are inflammable. It is in this case desirable that the solvents do not mix with water.

The **specific heat** and latent heat of evaporation must be low. Since in the course of the extraction the solvents are raised to their boiling point and then gasified and recovered by condensation, it is obvious that a larger amount of fuel must be burnt under the boiler to gasify a solvent with a high specific heat and latent heat than one with low ones, also a larger amount of water is required to condense the vapours again.

For the same reasons the **boiling point** must be as low as *possible*, except in the case of the extraction of bones and materials containing water. Here the use of a solvent boiling at a higher temperature than water is desirable, since at temperatures above 100° C. the water boils away, thus allowing the solvent to permeate the material freely and extract the fat.

Methods of Extraction

Benzine.—Two methods of extraction are employed:—

1. Extraction by cold solvents.
2. Extraction by hot solvents.

1. **Cold Extraction.**—This is preferable as regards fire insurance, and is largely practised with carbon disulphide for obtaining palm fats out of palm kernels. The crushed and warmed seeds are charged into A (Fig. 34) (one of a battery of

six closed iron cylinders) on to a perforated bottom F, covered with sackcloth, and a stream of carbon disulphide from a reservoir is allowed to percolate through, passing in by B and flowing away by L (which is provided with a strainer) into the next cylinder of the series. The solvent thus flows through each cylinder in order, from the top to the bottom, remaining for a short time in each before passing on into the next. The solvent leaves the battery charged with about 50 per cent. of fat. The exhausted cylinders are heated by a current of steam passed in through C, and the solvent still in the seeds is driven off through D, condensed in long tubes, and used again. The solvent containing the fats is pumped to the steam-heated still R, where the solvent is boiled off by the steam coils J, K (Fig. 35). The vapours rise through M, and the solvent is recovered by condensing the former in a special condenser. The residue of oil or fat left in R is freed from solvent by blowing steam through it, after which the oil is run off through P, and allowed to stand until the condensed water has separated out. The battery of vessels is so constructed that anyone can be made the last of the series, ready to be discharged and refilled with fresh meal, so that the process is a practically continuous one, the only time lost being in the actual refilling and discharging, which is effected by removing the clamped-down cover from A.

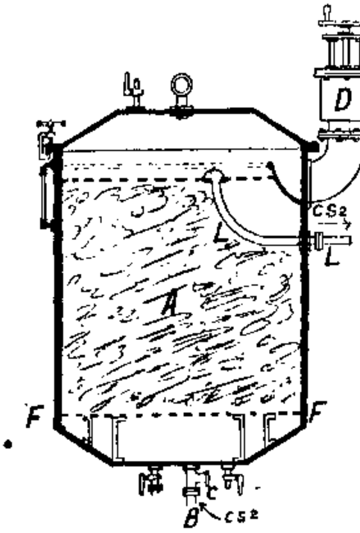


FIG. 34.—Cold Extraction Plant.

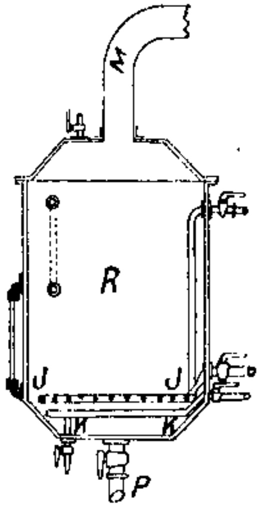


FIG. 35.—Still for Cold Extraction Plant.

The loss of solvent amounts to only 0.5 per cent. to 1 per cent. on 100 parts of fat. The fat is digested with a little concentrated sulphuric acid, and drawn off into wooden vessels. Fat obtained from carbon disulphide extraction is nearly odourless, whereas that obtained by this process from benzine still retains a slight odour of this solvent, and may be used for making soap.

Fig. 36 shows a typical cold extraction plant used for extracting grease from hides, or similar material which is spoilt by heat. Fig. 37 shows a photographic view of the plant. The skins are hung on a frame or "horse," and are run into the square extractors A, four of which are shown in series.

The benzine is then pumped from the tank B, by means of the pump C, into the extractors A, and enters at the top in the form of a fine spray. It then passes down over the material, extracting the grease in so doing. The fat-rich benzine passes from the bottom of the extractors and is pumped to the still D, where the benzine is distilled away in the usual manner and the fat left behind. In order to remove the last traces of benzine a current of live steam is usually blown through the residual fat.

The skins having been thus washed with benzine, it is now essential to dry them without using free steam, as this would damage the goods.

This drying is effected by hot dry air in the following manner:—Air is drawn out of the bottom of the extractors A by means of the fan F; this air then passes through the condenser G, where it is cooled, and benzine and moisture are deposited. The cooled air then passes on into a heater H, where it is warmed, and then once more passes into the extractor A, entering at the top, where the hot dry air once more absorbs a charge of benzine and moisture from the skin. It again is pumped away at the bottom of the extractors by the fan F, and the cycle is repeated until the skins are dry and benzine-free.

FIG. 37.—Cold Extractor Plant. General view of Scott's Degreasing Plant for skins, showing "horse" or frame for skins, and extractors' door.

This plant is used by hat manufacturers; for rabbit skins; also by tanners in making box calf and chrome leather.

2. **Hot Extraction.**—In this process the extraction takes place continuously with a limited amount of solvent charged once for all into the apparatus, which is merely an enlarged form of the Soxhlet extractor employed in the laboratory.

An apparatus extensively used for extracting fat from bones by means of benzine is illustrated below.

The degreasing boilers A, A (Fig. 38) are filled with air-dried bones which rest on the perforated floor *n*, *n*. The lower space B is heated by means of a steam coil *d*. By means of a nozzle *b* live steam can be blown in. Benzine is heated in the boiler C by means of a steam coil, and the benzine vapour, rising upwards, is superheated to 120°-130° C. in the tubular superheater D by means of high-pressure steam. The superheated benzine vapour issues from small holes in the tube *r*, and streams upwards through the bones. Part of the vapour condenses here, and flows down, carrying with it fat extracted from the bones, and collects in B, where it is continually boiled by means of the steam coil *d*. Part of the benzine vapour escapes in the gaseous state through *p*, and, together with the water simultaneously expelled from the bones, is condensed in the cooler E. The superheating of the benzine vapour

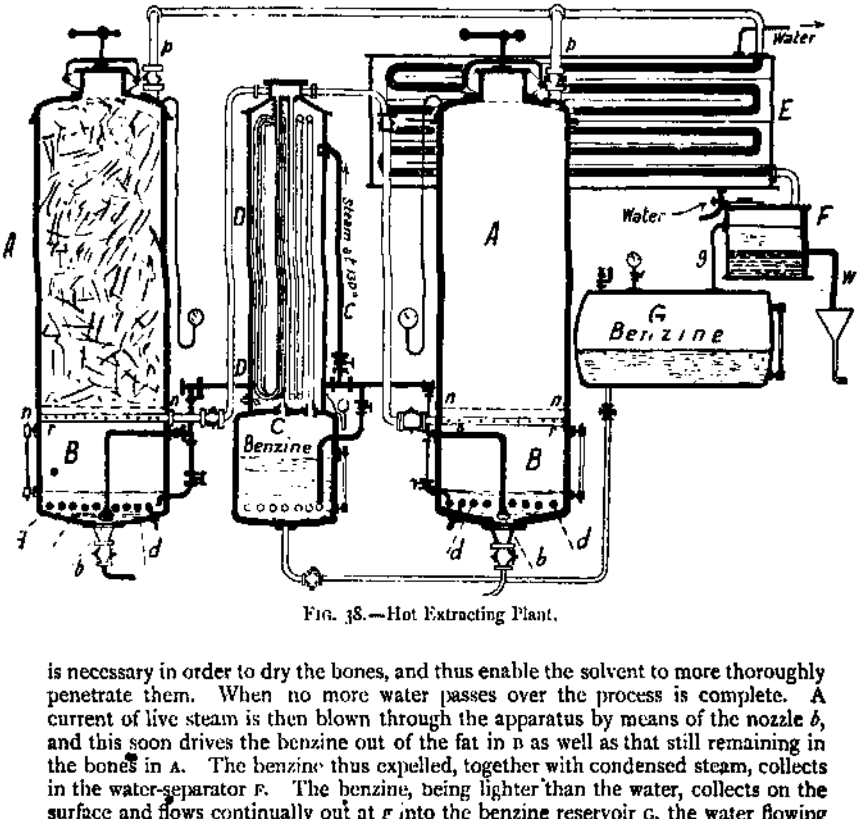


Fig. 38.—Hot Extracting Plant.

is necessary in order to dry the bones, and thus enable the solvent to more thoroughly penetrate them. When no more water passes over the process is complete. A current of live steam is then blown through the apparatus by means of the nozzle *b*, and this soon drives the benzine out of the fat in B as well as that still remaining in the bones in A. The benzine thus expelled, together with condensed steam, collects in the water-separator F. The benzine, being lighter than the water, collects on the surface and flows continually out at *g* into the benzine reservoir G, the water flowing away by *w*. From the reservoir G the benzine flows into the lower-situated vessel C, and is used over again.

It will be seen that very little benzine is necessary to effect extraction, the same benzine being used over and over again. Bones treated thus yield 6-7 per cent. of fat.

Fig. 39 shows a typical bone extraction plant made by Scotts, Kingsway House, London.

The material to be extracted is placed in the digesters or extractors 1 and 2, and is there treated with benzine or other volatile solvent. The digesters are supplied with steam coils, so that the solvent boils, the vapours passing along the pipes 3, 3, 3, through the tubular condensers 4 and 5, where the vapours are condensed by a counter-current of cold water, and the liquid solvent, free from grease, collects in the tank 6.

The separate water passes away first through a water separator (not shown in the figure), advantage being taken of the fact that there is a difference in the specific gravity of the two liquids, the benzine floating on the surface of the water, so that the water continually flows away at the bottom, as it comes over with the benzine.

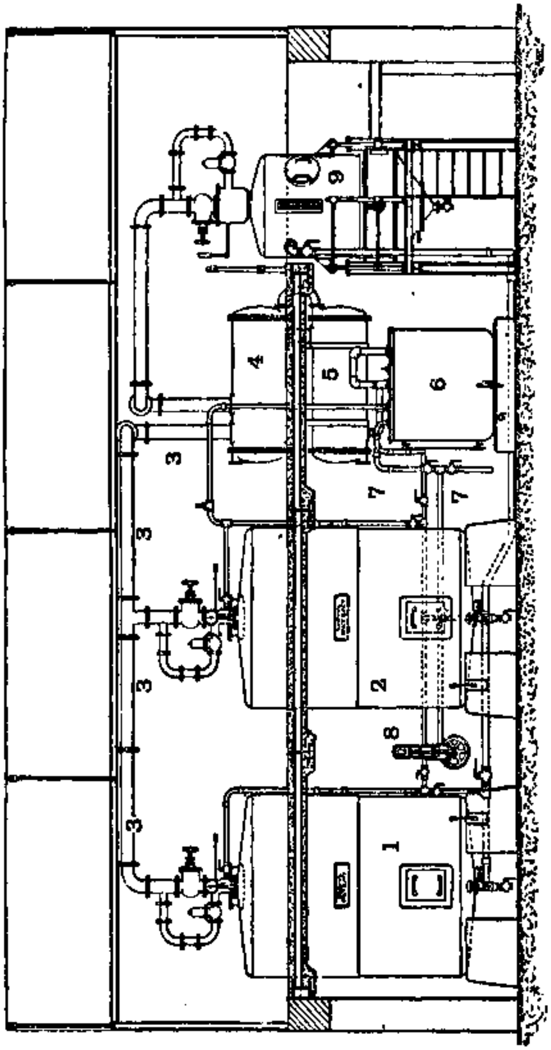


FIG. 39.—Bone Extraction Plant.
(Scott's, Kingsway House, London.)

The solvent is then pumped back from this tank to the extractors 1 and 2, by means of the force pump 8. There is thus a continual circulation of solvent over and through the matter to be extracted in the extractors.

Finally, when the extraction has proceeded far enough, the solvent, rich in fat, is pumped from the bottom of the extractors 1 and 2 into the still 9, and the last trace of solvent is then distilled away from the fat, the recovered fat in the still being finally steamed to remove the last trace

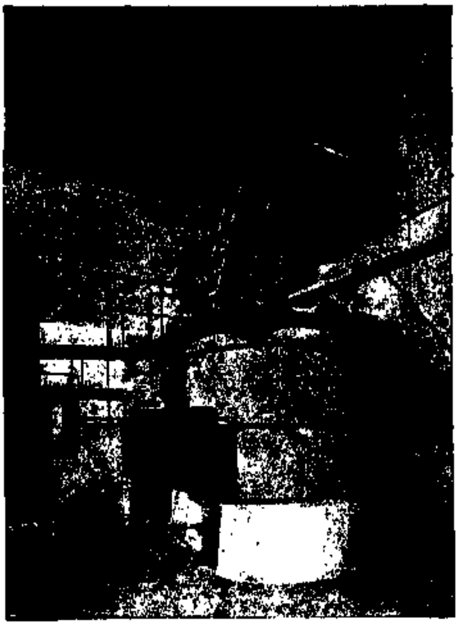


FIG. 40.—Solvent Extraction Plant for Bones. View of Extractors.
(Scotts, Kingsway House, London.)

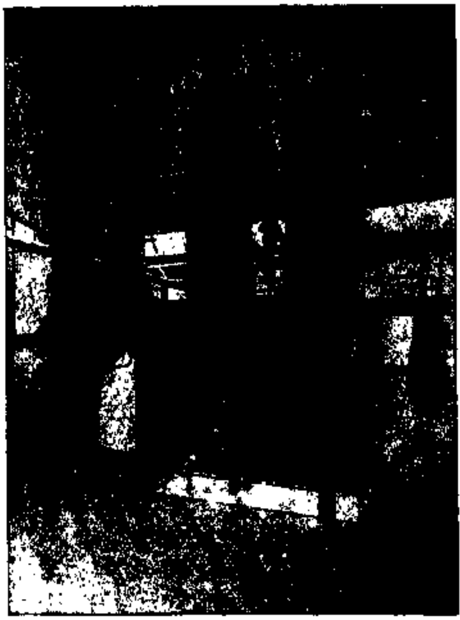


FIG. 41.—Solvent Extraction Plant for Bones. View of Condensers, Still, and Storage Tank.
(Scotts, Kingsway House, London.)

of solvent therefrom. The vapours from the still 9 are condensed in the tubular condensers 4 and 5, and the solvent is recovered in 6.

Any traces of solvent remaining in the degreased material left in the extractors 1 and 2 are recovered by steaming the charge in the extractors with "open" or direct steam, the mixed vapours coming from the extractor pass away to the condensers 4 and 5, and the condensate to the tank 6 *via* the water separator as before described.

The plant described is only suitable for material which retains its structural form under treatment, and does not tend to bind or break down into a sodden mass. Other materials require apparatus of special design, generally with agitating gear, to which some reference is made later.

The same plant is shown photographically, with slight modifications, on p. 71. Fig. 40 shows the extractors with the elevator for conveniently charging them, while Fig. 41 shows the condensers, still, pump, and solvent store tank.

A more modern plant, fitted with agitators, is shown in Fig. 42. It is used for extracting oil from seeds. The seeds are first ground into a meal, which is placed in the extractors 1. Here they are subjected in succession to three operations, viz.: (1) washing with hot liquid benzine; (2) treatment with hot benzine vapour; (3) steaming to remove benzine.

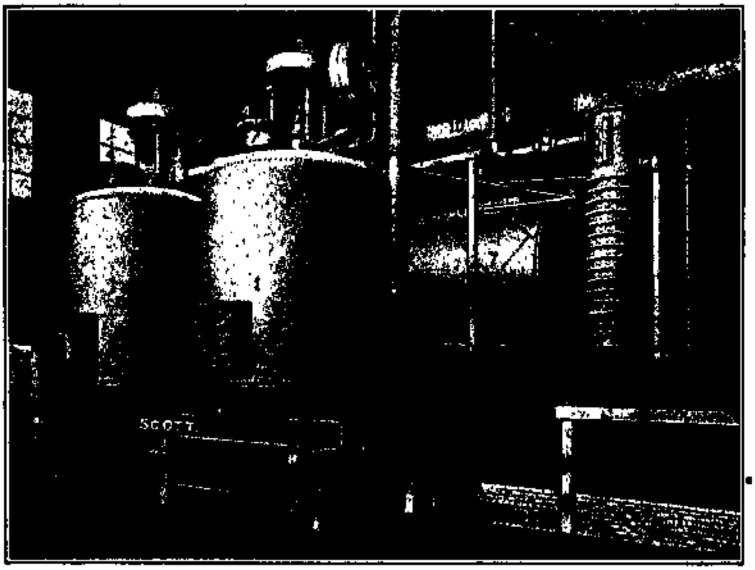


FIG. 42.—Extraction Plant with Stirrers for Oils from Seeds.

(Scotts, Kingsway House, London.)

1, Extractors; 2, Vaporiser; 3, Vapour pipe; 4, Charging hole; 5, Discharging door; 6, Stirrers; 7, Benzine storage tank; 8, Multiple still; 9, Feed tank for still; 10, Condenser; 11, Water separator.

1. **Hot Washing with Benzine.**—The benzine is pumped from the storage tank 7, through a **heater** (not shown, but situated behind the extractors 1), to the top of the extractors, the hot liquid thus filling the extractors completely, and, percolating down through the mass of meal, dissolves out the oil. The liquid is pumped away from the bottom of the extractors up into the feed tank 9. From here it is fed down in a continuous stream into the still 8, which is of a special construction, composed of a number of trays, similar to an ammonia still (see Martin's "Industrial Chemistry: Inorganic," Vol. II.). Here the benzine is continuously distilled away from the oil, the benzine vapours being condensed in 10, whereas the oil runs out continuously at the bottom of the still.

Consequently the oil is only heated for a short time, and so it is of an excellent quality. Prolonged heating is detrimental to the colour of oil.

2. **Treatment with Benzine Vapour.**—After the hot washing of the ground meal with the benzine comes a further treatment with benzine vapour. The benzine vapour is produced in the vessel 2, shown under the extractor 1, the benzine being here heated by steam coils until it boils, the vapours passing up through a pipe (not shown) at the back of the extractor 1, and then out at the top; the vapours pass downwards through the meal, then traverse the pipe 3, which carries them to the condenser 10. The benzine condenses here, together with water evolved from the seeds. The mixed liquids pass into the water separator 11, and the benzine passes on into the storage tank 7, the water running to waste.

3. **Steaming to Remove Benzine.**—After the treatment with hot benzine steam is blown through the residues in the extractor 1, in order to remove the last traces of benzine. The steam and benzine are condensed by 10, separated by 11, and the benzine stored in 7 as before.

Method of Working the Plant.—A diagrammatic section of the plant is shown in Fig. 43, as adapted for extracting oil from seeds. The ground seed meal passes along the conveyor A and falls into the storage bins B. From here the charge can be placed into the extractors D through the charging hole C. The extracted charge is removed through the door E in a dry condition. The extractor D is provided with an agitating shaft 1, driven by means of a belt pulley 2, worm and worm-wheel. The extractors D are in duplicate, so that one can be working while the other is charging. In order to introduce solvent from the store tank J into circulation, and to wash the seed meal in D with **hot liquid solvent**, the valve 6 is shut, and the valves 18 and 19 are opened. The solvent from J is then allowed to flow down the pipe 20 to the vaporiser F. This is a steam-heated tubular boiler. Part of the solvent is here vaporised, and passes up the pipe 7 into the extractor D, while part of the hot solvent in the form of a hot liquid flows out at the bottom of the vaporiser F through 8 along 9 into the pump K, which lifts it up the pipe 10, along the pipe 21, into the top of the extractor D. The hot liquid solvent passes down through the meal, extracts the oil therefrom, and flows away from the bottom of the extractor through the pipe 4 and sight glass 3, through the valves 22 and 23, *via* the pipe 9 into K again, and thence back once more *via* pipes 10 and 21 into D, so that in this way the meal in D can be washed with **hot solvent**.

In order to wash with cold solvent (which is sometimes required) the vaporiser F must be cut off. To do this the valves 6 and 18 are closed, and the valves 19, 22, and 23 are opened. The solvent and its dissolved oil passes out from the bottom of the still, and reaches the pump K, passes through the pipe 21 to the top of the extractor D, down through 4, 22, and 23, along 9 into the pump K again, so that a cold extraction is possible with this plant.

In order to treat the **meal with solvent vapour** the valves 6 and 18 are opened. The solvent, containing the oil, flows away from the extractor D through the pipe 4 and the sight glass 3, through the pipe 5 and valve 6, into the vaporiser F. Part of the solvent is here vaporised, the vapours, passing up the pipe 7, enter the extractor D at the top.

The remaining portion of the solvent, containing the dissolved oil, runs away from the foot of the vaporiser F through the pipe 8, and flowing along the pipe 9 reaches the pump K, which lifts it up through the tube 10 to the still feed tank L.

From here it flows by the pipe 11 through a tubular "heater-condenser" or "heat-exchanger" N (in which it is heated by vapours coming from the still M, which it serves to partially condense), and from N it flows *via* the pipe 12 into the continuous still M. Here it passes down the still, and in so doing is completely deprived of solvent by a counter-current of steam, the oil flowing away continuously in a solvent-free condition at the bottom of the still. The solvent vapours pass up by the pipe 13, and passing through the tubular condenser N are partially condensed by the counter-current of liquid flowing from L to the still; the heat thus abstracted going to lighten the work of the still by preheating the incoming liquid. The partially condensed vapour is completely condensed in the two tubular condensers G. Here steam derived from the still and from the water in the meal is also condensed. The solvent and water flows from G through 15 into the water separator H. The water flows out below through the siphon tube 16, while the solvent flows away from 17 into the solvent store tank J, when it is ready for reuse.

When the extraction of oil from the meal is nearly completed, the solvent drawn off from the extractor is very poor in oil. This poor liquid is not sent down the still, but pumped to a "half-spent" solvent tank and reused as the first charge of solvent for a fresh charge of meal.

When the extraction of the meal is completed traces of solvent must be removed by steaming. To do this the valves 6 and 24 are shut, and the valve 25 is opened. Dry steam (not superheated) is then let into the extractor D through the valve 25, and this steam, blowing through the meal, removes all traces of solvent therefrom. The steam and solvent vapour pass up the pipe V into the condensers G, and traverse the water separator H, the separated water running to waste, while the solvent benzine passes into the storage tank J. Finally, the doors E of the extractors D are opened, and the meal, now quite dry, is removed and fed directly to cattle or horses.

Very little labour is required to work the plant, two men operating the largest sizes. The economy of steam consumption is considerable, the coal required per ton of raw material being 2-3 cwt.

The loss of solvent works out on the average as 1½ gallons per ton of material treated.

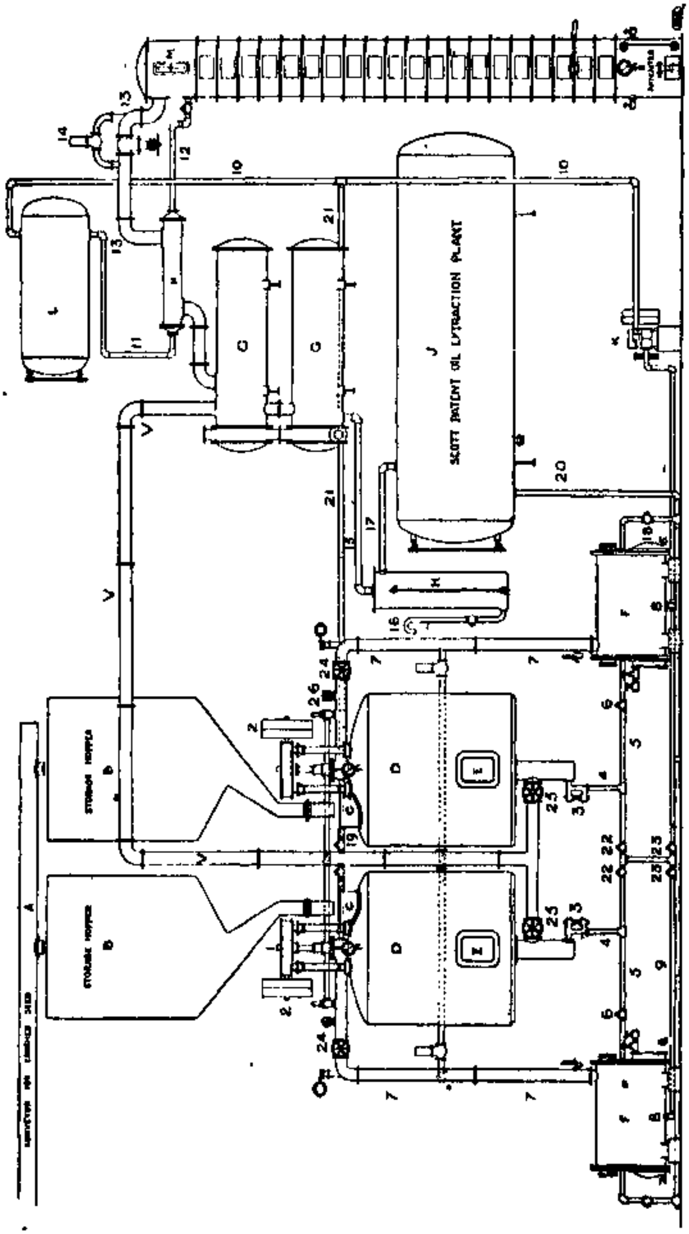


FIG. 43.—Scotts Extraction Plant for Seeds.

For making estimates the benzine loss can be put as ¾ per cent. of the quantity of material extracted.

The benzine used should boil between 90°-110° C., but the range 100°-125° C. is often used.

Merits and Demerits of the Methods of Extracting Oils and Fats by Pressure and by Solvent

1. Edible oils and fats are not usually prepared by extraction by solvents, since enough solvent is usually retained to impart a nauseous taste. Such oils and fats are, therefore, usually used for soap-making and other technical purposes.

Improvements in plant, and especially in the manufacture and careful distilling of solvents, are stated to have overcome this difficulty in many cases, and edible cocoa-butter and other fats and oils are stated to have been prepared by extraction processes alone.

Indeed there are a number of plants at work in England using the chemical solvent extraction process for producing edible oils used in the manufacture of first-grade margarine.

2. The solvent process extracts the fats and oils to a far larger extent than the pressure process, only about 1 per cent. of oil being left in the extracted seed, about 7-10 per cent. in the pressed. In many cases a combination of pressure and solvent processes is the best, oil being first expressed and sold as edible oil, and the residue, still fairly rich in oil, is extracted, and the oil thus obtained sold for soap-making and other technical purposes.

3. Extracted meal has been stated to be unsuitable for feeding cattle. This, however, is incorrect, since large quantities of extracted meal are now used both in England and Europe for feeding cattle. It is usually mixed with press cake, bran, or other material, and fed to the cattle.

Press cake, containing 6-10 per cent. of oil, is obviously a richer food than extracted meal, but it is certain that a high percentage of oil in cake has not quite the value that it was formerly believed to possess. Extracted meal is richer in albuminoids than press cake, and albuminoids are regarded as the flesh-forming element in food.

At the present time, however, seeds such as linseed and cotton are usually crushed and not extracted, because a considerable demand exists for linseed and cotton-seed press cake containing a considerable percentage of oil, this being considered a valuable cattle food. Extracted linseed or cotton-seed, on the other hand, cannot readily be sold as a cattle food, although it is doubtful (as above mentioned) whether this is due to mere prejudice, or whether it is founded on actual experience.

4. The solvent-extraction process has great claims for attention when the press cake or residue is not suitable for a cattle food, and the main object is to obtain as great a yield of oil as possible. This happens, for example, with rape seed and castor-oil seed, the residues of which are only suitable for manure.

Extracted meal is better than press cake as a manure. It has been proved that the presence of oil in a manure is detrimental, as it prevents the manure being readily assimilated by the soil, and defends the fertiliser from the attacks of the soil organisms which convert the constituents of the fertiliser into immediate soil foods.

Press cake, in addition to possessing the defect of containing oil, has to be broken up before it can be applied as a manure.

Extracted meal, on the other hand, is already in a broken condition, and so is readily applied as a manure, and has little oil in it.

5. The solvent-extraction process has often been recommended for extracting seeds fresh at the place of production, thus saving the deterioration which invariably results when the seed is shipped long distances. In this case the residues are used on the spot as manures, while the oil alone is shipped, thus saving freight.

6. The plant required for the solvent process is comparatively simple and inexpensive, as compared with the crushing process. Only a small amount of power is necessary for driving the plant, and the labour required need not be highly skilled.

7. It should be noticed, however, that the oil seed crusher charges for the percentage of oil left in the cake at the same price as if it were separated from the seed. Consequently, it does not matter to the oil seed crusher how much or how little oil he leaves in his cakes.

He gets the same price for the oil whether he leaves it in the cake or whether he recovers it. Hence by extracting more oil by solvent he would not realise more money for the oil originally contained in the seed, and indeed he would lose if he did not succeed in selling his extracted meal as a cattle food.

It is obvious, therefore, it is a matter of close study which process—the solvent extraction or the pressing process—should be adopted in practice, as several factors are involved.

CHAPTER VIII

The Refining and Deodorisation of Animal and Vegetable Oils

CHAPTER VIII

THE REFINING AND DEODORISATION OF ANIMAL AND VEGETABLE OILS

Nature of Impurities to be Removed in Refining

Oils pressed in the cold from quite fresh seed require little or no refining.

When the oils are hot pressed changes are produced by the heat on the oil while still contained in the plant cells, and as a result the oils acquire a more pronounced taste and odour and a darker colour. These effects are probably produced by **albuminous substances** getting into the oil—either in the form of a fine suspension or actually dissolved in the oil.

In the case of animal oils or fats a low temperature of rendering and perfect freshness of materials are the essential conditions for obtaining a fine product. The impurities causing a bad taste, smell, and odour are also probably of an **albuminous character,** or decomposition products of them. The presence of free **fatty acids** in the oil causes an unpleasant taste—the so-called rancid taste—and anything more than 0.1 per cent. free fatty acid must be removed in order to make the oil "neutral" tasting.

General Methods of Refining and Bleaching Oils and Fats

The actual process adopted depends somewhat upon the nature of the oils. If these are fresh and well made, they may be worked up directly into technical products without any refining.

The presence of free **fatty acids**—causing rancidity—in the oils is easily removed by treating with alkali (see below) and removing the resulting soaps by washing. The removal of the **albuminous matters,** however, is a more difficult problem.

The following are the chief methods employed for refining oils:—

1. **Heating the Oils.**—The temperature must be sufficient to coagulate and destroy the albuminous matter, without affecting the oil.

A heat treatment is often applied to linseed oil (which see below).

2. **Steaming the Oil.**—Either superheated or wet steam is blown through the oil, sometimes in a vacuum and sometimes under ordinary pressures. Volatile odorising principles are thus carried away, and the albumen coagulated.

Medicinal castor oil and some edible oils are said to be refined by this method.

3. **Cooling the Oils.**—According to German Patent, 163,056, and English Patent, 10,326, 1905, albuminous substances are precipitated to some extent when liquid oils are cooled. Obviously this method can only be employed in the case of oils that will not easily solidify.

4. **Treating with Fuller's Earth, China Clay, Decolorising Carbon, etc.**—From 0.2-10 per cent. of fuller's earth may be employed, and the whole is agitated and heated (below 80° C. for edible oils) for ten to sixty minutes, and the whole purified through a filter press. See p. 90. Decolorising carbon is more expensive than fuller's earth, and for oils is not more effective.

5. **Oxidising the Oil.**—Albuminous impurities and colouring matters in oils are more readily oxidised and destroyed than the oils, so that it is possible to bleach many oils by oxidation without

appreciably oxidising the glycerides. The free fatty acids in the oil are always increased by this treatment.

The following oxidising agents are employed :—

(*a*) **Air.** See p. 89, bleaching of palm oil.

(*b*) **Ozonised air.**

(*c*) **Peroxides, persulphates, percarbonates, perborates.**

(*d*) **Sodium nitrate.**

(*e*) **Sodium and potassium bichromate.**

(*f*) **Nascent chlorine** (from bleaching powder or sodium dichromate and sulphuric acid). The nascent chlorine acts as a bleaching agent by its oxidising action :—

$$2Cl + H_2O = 2HCl + O$$

6. **Reducing the Oil.**—Sulphur dioxide sometimes bleaches oils by reducing the colouring matter in them to colourless substances. "Hydrosulphites" and formaldehyde hydrosulphites have been used under names such as "Formaldehyde-sulphoscylate," "Hydraldite" (sodium hydrosulphite and ammonia), etc. See English Patents, 11,983 (1906), 16,260 (1909), 12,157 (1911), 21,359 (1911), 22,453 (1911), 3,433 (1912); French Patents, 410,824, 431,294; German Patents, 195,663, 214,043, 223,419, 224,394.

"Hydrogenation" (see Chap. IX.) of oil (hydrogen and a catalyst) decolorises and deodorises an oil by reducing it, but here, unfortunately, the oil is at the same time "hardened."

7. **Charring Albuminous Matters by Dehydrating Agents.**—**Sulphuric acid** acts on albuminous matters, charring them by the removal of the elements of water. The charred matter, on settling, carries down most of the impurities in suspension. The oil itself will be attacked if the acid be too strong or the temperature too high.

A concentrated solution of **zinc chloride** (sp. gr. 1.60-1.65) has a charring effect on albuminous matters, similar to that of sulphuric acid, but is expensive to use.

8. **Action of Soap Solutions.**—When free fatty acids are neutralised in oils by alkali, the resulting soap solutions on separation entangle and carry away many of the impurities.

9. **Bleaching by Light and Actinic Rays.**—Direct sunlight is a powerful bleaching agent. Diffused daylight also bleaches, but more slowly. The action of light, however, is slow, so it is only used in practice for the finest oils, *e.g.*, poppy, linseed, and walnut oils for artists, salad oils, medicinal castor oils, etc. The oil is exposed to light in shallow trays covered by glass, or in flat bottles. White beeswax, white cocoa-butter, etc., can be prepared this way.

Many patents have been taken out for exposing oils and fats to actinic rays or ultra-violet light from the Cooper-Hewitt mercury vapour lamp and the Uviol lamp. See German Patents, 195,663, 223,419.

Practical Details of Technical Methods for Refining Oils

Tanking and Filtering.—The oils are run into tanks and allowed to stand. Dirt and impurities settle to the bottom, and the supernatant oil becomes clear. Sometimes oils are tanked for months or years at a time (*e.g.*, linseed oil).

A much quicker process is direct filtration, which avoids the loss of time and storage space necessitated by the old plan of subsidence, the sole product of the oil mill being a cake and bright oil, the residue in the filter being worked back again in the mill. The filtration is effected by pumping the oil direct from the hydraulic presses through a **filter press** (Fig. 44). This consists of a series of grooved iron plates, hollow on the inside, which are clamped tightly together, and which contain cloth separating them. The oil is thus forced through a succession of cloth filters, and the solid matters are caught and deposited in the spaces between the cloths. Nothing but oil comes in contact with the plates, the oil passing out at the end pure and bright.

There are two distinct types of filter presses :—

(1) Recessed frame with centre feed.
(2) Plate and frame type.

Fig. 44 shows a **recessed frame filter press type with centre feed.** In presses of this type the plates are made with raised edges, so that when they are placed together in a horizontal series, as shown in Fig. 44, each pair of plates encloses a chamber. The filter cloths are hung over both sides of the plates and are gripped by the raised edges. In this way the cloths make an efficient joint between the plates.

The usual way of inserting the filter cloths is shown in Fig. 46. Usually double filter cloths are used. These are joined together at the centre as shown in Fig. 46, A, and in order to insert them one half of the cloth is rolled up and passed through the centre hole, and then both halves are spread out to cover each side of the plate. See B, Fig. 46.

Sometimes, however, two separate cloths are used, with a centre hole in each. They are each secured at the centre hole by bayonet or screw clips, illustrated in Figs. 46, 47.

In the recessed type of filter press the liquid to be filtered enters through the centre hole, passes up into the chamber between the two plates, and then filters through the cloth covering the plates on to the grooved channels on the plate, runs down the grooved channels, and away through an outlet at the side of the base of the plate. The outlet hole is shown in Fig. 45 and Fig. 46, C.

The recessed plate presses are used when the material to be filtered does not form a solid cake. After the press has been opened, the cakes are easily made to fall out on to a conveyor, truck, or other arrangement beneath the press.

This type of filter press is also used when dealing with materials liable to clog the passages.

Cakes, however, cannot be efficiently washed in presses of this type, as there is always a centre core of material throughout the length of the press which cannot be reached by the wash-water.

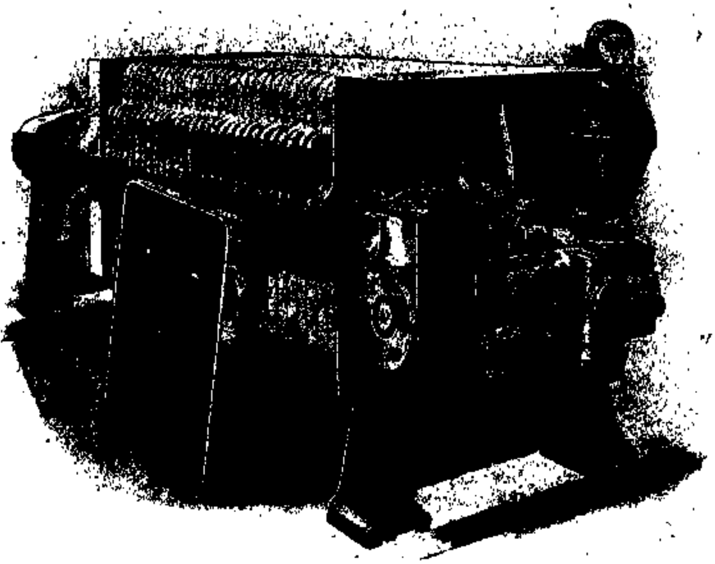


FIG. 44.—Hydraulic Oil Filter Press, with self-contained Steam Pump.

(Rose, Downs, & Thompson, Hull.)

Recessed Frame with Centre Feed.

Fig. 49 shows a **plate and frame type of filter press** by Manlove, Alliott, of Nottingham. In this type of press the plates are made without raised margins, and the grooved portion is therefore flush with the rim. The chambers are formed by the insertion of frames (Fig. 50) between each pair of plates, and the filter cloths lie between the plates and the frames.

The feed passage for the liquid is arranged on the border of the plates, with ports leading into the interior of the plates. The material filtered off in the frames can be easily and thoroughly washed.

For this purpose the plates and frames are arranged with the channels for feed inlet, wash-water inlet, wash-water outlet, air outlet, and a separate outlet (or outlet tap on each plate) for the filtrate. Usually the channel for wash-water inlet is made at the bottom of the plate and frames; the three

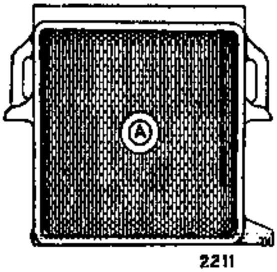


Fig. 45.—Recessed Filter Plate showing centre feed A and outlet hole on left.

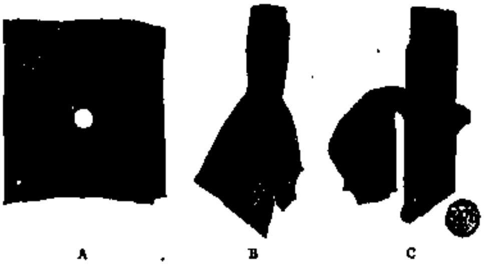


Fig. 46.—A is double Filter Cloth. B is same rolled up for insertion. C shows side view of recessed filter plate, showing mode of insertion of the cloth and outlet hole at side.

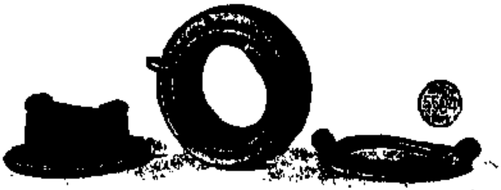


Fig. 47.—Bayonet Clips for Filter Cloths, centre feed.

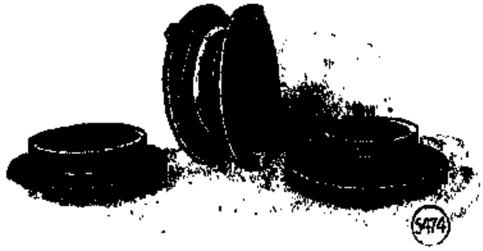


Fig. 48.—Screw Clips for Filter Cloths, centre feed.

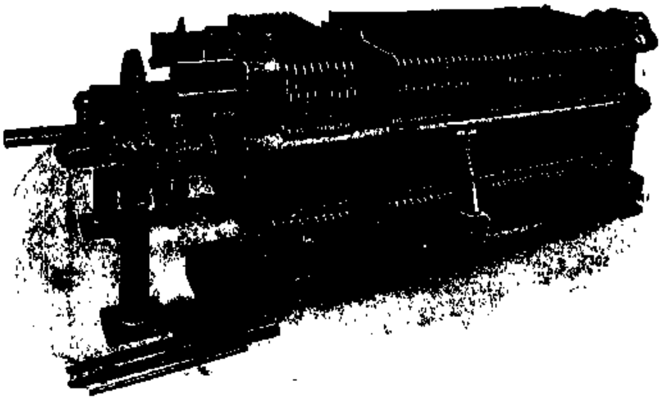


Fig. 49.—Plate and Frame Type of Filter Press.

(Manlove, Alliott, of Nottingham.)

channels for feed inlet, wash-water, and air outlets at the top, and the filtrate outlet at the bottom corner opposite the wash-water inlet.

The material to be filtered enters the chambers by means of a port in each frame from the feed inlet. The wash-water inlets and outlets, also the air outlets, are arranged so that the port to the chamber is made only in alternate plates.

The water enters behind the cloth on one side of each cake, expels any contained air, passes evenly through the cakes, and away by the special outlet channel on the opposite side of the cake to which it enters. A siphon pipe is often placed on the wash-water outlet at the top of the press to assist drawing the wash-water through the cake.

Plate and frame presses are used when the material to be filtered will form a solid cake. The whole cake collects in the frames, and can be taken right out in the frames, removed, and stored without breaking up. Plate and frame presses are also used if the cakes are to be thoroughly washed, or if cakes of a thickness over 1½ in. are required. Instead of washing, the material can be steamed, or dried in filter presses by hot air. Occasionally, filter presses are fitted with plates heated by steam passages, so that the substances can be filtered hot.

Filter presses range in size from six to fifty chambers, with plates from 12 in. square to 40 in. square. The thickness of the cakes vary from 1 to 2 in. The output varies very much with the nature of the oil to be filtered.

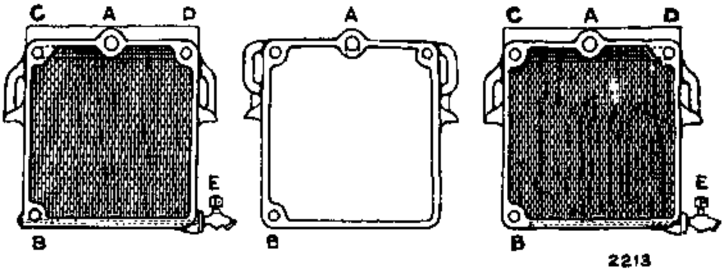


Plate. *Intermediate Frame.* *Plate.*

FIG. 50.—Parts of Plate and Frame Filter Press.

A, Feed inlet.
B, Wash-water outlet.
C, Air outlet.
D, Wash-water outlet.
E, Outlet for filtrate.

Thus, a twenty-four chamber press with plates 25 in. square (total filtering area 208 sq. ft.) will filter in twenty-four hours about 16 cwt. of castor oil, 70 cwt. of crude rape or stale olive oil, 100 cwt. of crude cotton oil, and 140 cwt. of coco-nut, fresh olive oil, or linseed oil.

With linseed oil a press will run a week without being opened for cleaning. With castor oil a much shorter time of running is necessary. Oils are filtered hot more rapidly than cold.

Potter's Oil Filtration Plant

A very simple and efficient device for filtering oil is often used and illustrated in Fig. 51.

The oil is fed into a crude oil receiving tank fitted with a 2-in. gun-metal cock at the bottom. From here it runs down into a tinned iron tank which is provided with nozzles to which are fastened filter bags, shaped like tubes, as illustrated. The oil flows through the filter bags and drains away into a tinned iron oil catcher, and thence into a filtered oil tank.

This plant works rapidly and is inexpensive. It is stated that it will filter in a day of twelve hours:—

Palm oil, 4 tons; nut oil, 6 tons; soya oil, 8 tons; linseed oil, 12½ tons; cod-liver oil, 4 tons.

The apparatus is placed on the market by James Potter, Sculcoates Sheet Metal Works, Hull, England.

Turbine Centrifugal Oil Filter.—This form of filtration has been coming into vogue of late years. Fig. 52 shows an oil filter placed on the market by the Industrial Waste Eliminators, Ltd., of London.

It consists of a rapidly rotating centrifugal basket, covered with a filter cloth. The basket revolves about 2,500 revs. per minute. The oil to be filtered is run in a continuous stream from a storage tank or pipe line through the funnel A fixed to cover B of casing C into the hollow spindle D, carrying the metal cone E with wire basket F and filtering medium G, which are being revolved at high speed by means of turbine H actuated by steam through nozzle *h*.

By the centrifugal action the liquid is forced through holes *d*, passing through the filtering medium, which retains all solid and suspended matter, and the oil and water travelling up the cone is thrown through perforations *e* on to the steam jacket I, previously raised to the desired temperature. The water, either free or in emulsion, is vaporised, the vapours passing through holes *b* in the cover, the pure oil running down the jacket and through the filtered oil outlet J, either into a storage tank or conveyed through a pipe line to any desired place.

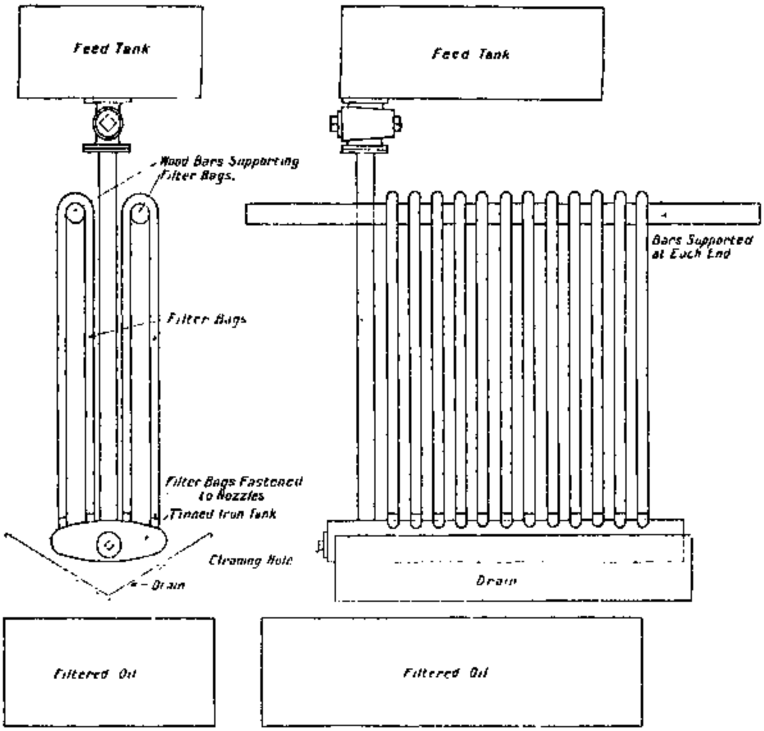


FIG. 51.—Potter's Oil Filter.

Such a filter will produce from 10-50 gallons of filtered oil per hour, the exact quantity depending upon the nature and quality of the oil. To obtain a greater output a number of units must be connected up in multiples.

Treatment with Caustic Soda.—The oil is washed in special tanks with a solution of caustic soda or sulphuric acid. Thus *cotton-seed oil* is pumped into a large tank (shown in Fig. 53, p. 86), then heated by steam to 30° C., and the proper amount (which depends upon the quality of the oil) of caustic soda solution (74° Bé.) run in and mixed thoroughly either by mechanical agitators, or by a current of air blown through the liquids for fifteen minutes. On standing, a sediment of coagulated albuminous and mucilaginous matter from the oil settles at the bottom of the tank, together with the excess of caustic soda solution. The oil is cooled and siphoned off from the sediment to a finishing kettle, where it is washed free from caustic soda by a stream of water. The wash-water is withdrawn from the bottom of the kettle until oil comes; then fresh water is added, and the process repeated until the oil is free from alkali. During this operation a blast of air is blown through the liquids, or mechanical agitators are used, in order to thoroughly mix the oil and water.

Finally, moisture is expelled by heating the oil gently by steam pipes to a temperature not higher than 50° C., while a current of air is blown through. The last traces of moisture are sometimes removed by adding plaster of Paris and filtering. Filtration through a layer of common salt also removes all moisture.

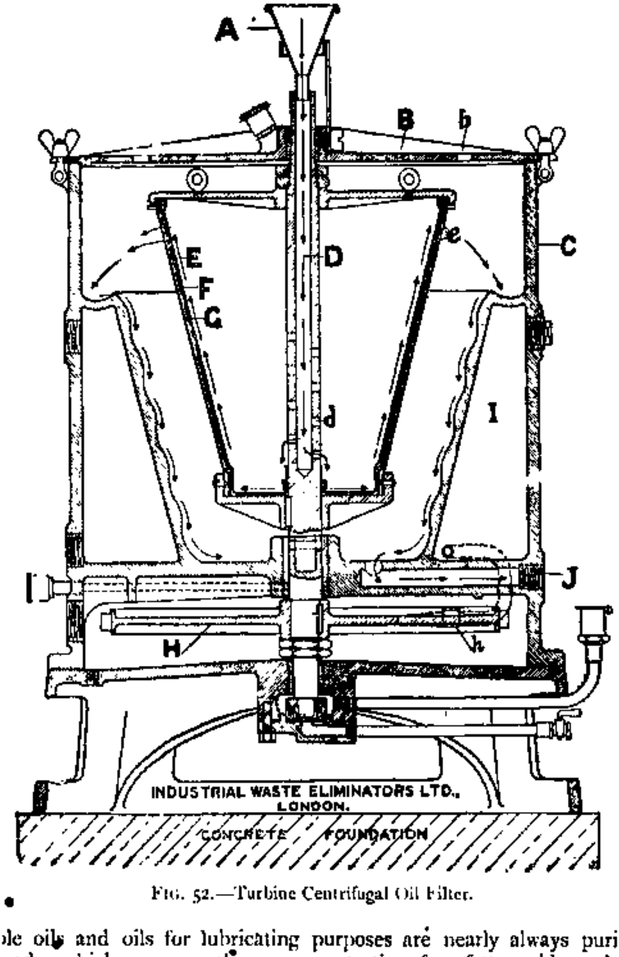


FIG. 52.—Turbine Centrifugal Oil Filter.

Edible oils and oils for lubricating purposes are nearly always purified with caustic soda, which removes the nauseous-tasting free fatty acids. A trace of mineral acid spoils the oil for lubricating purposes.

Deodorisation of Edible Fats.—Certain high-grade edible fats and oils are sometimes extracted with alcohol. They are stated to be rendered perfectly odourless and tasteless by this process, and so can be employed in the manufacture of high-class margarine and similar comestible fatty products.

Two methods are well known for the deodorisation of coco-nut oil:—(1) **Washing out the odoriferous bodies with alcohol.** This removes the fatty acids, and also such substances as phytosterol. *Chevreul* and *Schlinck* employ a joint process of washing with alcohol followed by treatment with charcoal. For a recent patent see **Urbain** and **Friege** (French Patent, 961,966, 1905). (2) **Volatilisation by steaming.** Jeserich and Meinert (1882) passed high-pressure steam at 6.8 atmospheres into the fluid oil for two to three hours; the non-volatile fatty acids left were then removed by adding 0.25 per cent. of calcined magnesia, and the magnesium soap formed is then skimmed off the surface. Kilmont (English Patent, 3,164, 1902) neutralises the oil with alkali before treating with steam. See also p. 129, under Cacao Butter.

Refining and Deodorising Plant for Edible Oil.—Fig. 54 shows a complete oil refining plant erected by Messrs Manlove, Alliott, Ltd., of Nottingham, England. It has a capacity of from 3-4 tons per charge, and is the usual size adopted by present-day manufacturers as a unit, any increasing output necessitating the use of additional units. The mode of working is as follows:—

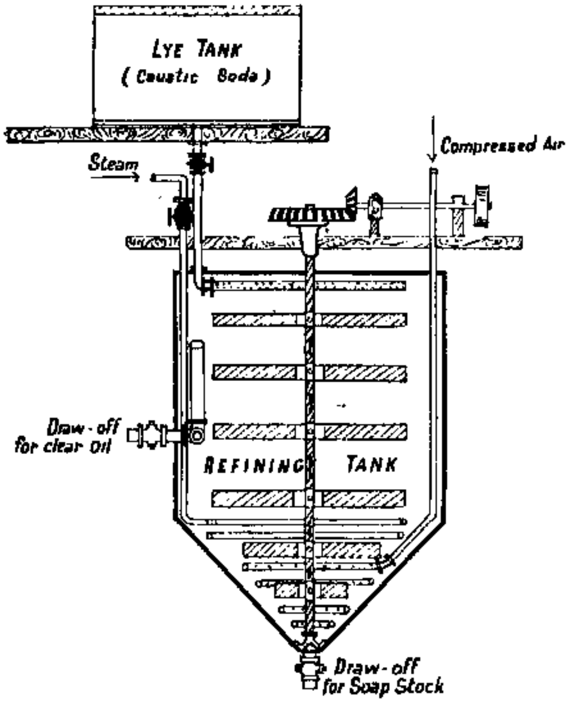


FIG. 53.—Cotton-Seed Oil Refining Tank.

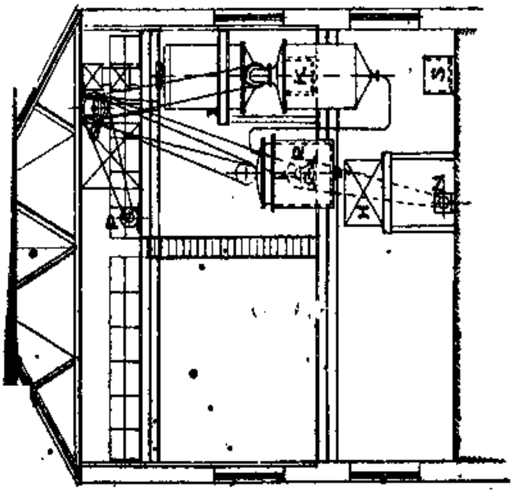
The oil is pumped from the crude oil store into the supply tank B. This is fitted with a heating coil, so that time is saved by preheating the oil before passing it on for the next operation. From B the oil gravitates into the neutralising or refining tank D, where it is heated to a suitable temperature. A sample of oil is withdrawn at this stage, and the fatty acids in it are estimated. Then the calculated amount of caustic soda solution is run in from a caustic soda tank C, the oil being the while agitated while the caustic soda is being added.

In modern practice two caustic soda tanks are employed. In the one a fresh solution of caustic soda is being prepared for use with a fresh batch of oil which is preheating in B, while the caustic soda in the second tank is being used for neutralising the oil in D, so that the process of neutralising proceeds practically continuously, and no time is lost in making up the solutions and in heating the oil.

Instead of caustic soda sodium carbonate is also used.

The treated oil is next separated from the soapy solution, and the oil run into E and washed with water until free from soap and alkali.

REFERENCE TO PLANT.	
A	CRUDE OIL PUMP.
B	CRUDE OIL SUPPLY TANK
C	2 CHEMICAL TANKS.
D	REFINER.
E	2 PRELIMINARY STILLS
F	2 PUMPS FOR FILTER PRESSES
G	2 FILTER PRESSES
H	FILTERED OIL TANK.
J	PRE-HEATER.
K	FINISHING STILLS.
L	OIL COOLER
M	CONDENSER
N	2 VACUUM PUMPS.
P	ELECTRIC MOTOR.
Q	LINE SHAFT
R	HIGH SPEED COUNTERSHAFT
S	3 SOAP TANKS



To face page 86.

The aqueous liquors are run off below.

The soapy washings thus drawn off are usually concentrated, and the soap contained therein recovered. For this purpose fresh alkali is usually added to convert the emulsified oil contained in the washings into soap. Sometimes the mass is acidified, and the resulting mixture of oil and fatty acids is separated and distilled and used as a white candle material.

A long time is usually required for the oil and soap to separate out in the settling tank, as difficulties due to emulsification of the oil ensue. In some firms brine is used to break down the emulsification. In other firms a rapid centrifugal motion is said to be used to effect separation.

Some firms filter press to separate solid soap from the oil.

The oil is then warmed in the closed vessels K under a vacuum, and so thoroughly dried. Then a charge of fuller's earth, floridene, or similar bleaching material is added, the oil agitated, and then filtered through the filter presses shown.

With some oils it is possible to take the oil from the filter press direct from the neutralising tank D without the use of the preliminary stills B, but this is hardly to be recommended if high-class edible oils are desired.

The oil is now run into the preheating still J. The oil is here heated under a vacuum, and the last traces of water removed.

The vapours from the still used in the next operation, namely, the deodorising or finishing still, pass through the heating pipes in the preheating still J, and thus economise time and fuel in the process of raising the oil in J to the right temperature for the succeeding process.

When the right temperature is attained, the oil is run from J into the deodorising or finishing still K, and it is there treated with superheated steam under a vacuum so as to remove the last trace of fatty acids, and leaves the oil perfectly free from any taste or smell.

Treatment with Sulphuric Acid.—Many industrial oils are purified in the same way as described above (caustic soda), but with a solution of **sulphuric acid.** About 2 per cent. of sulphuric acid of 66° Bé., mixed with an equal volume of water, is run into the oil contained in a lead-lined tank, which is preferably of a conical shape at the bottom to facilitate the separation of the acid sediment ("foots"). The tank is provided with a "closed" steam coil, and also an "open" air coil for agitating with compressed air.

The liquid is agitated by an air blast, warmed for about one hour, settled, and the acid run off at the bottom, and the oil washed with water and caustic soda until free from acid; finally the clear supernatant oil is decanted and filtered.

Different kinds of oil require different amounts and different concentrations of sulphuric acid; in most cases the necessary quantities can only be ascertained by actual trials. One to three per cent. of acid are the usual quantities. If the acid used is too concentrated, the oil is badly discoloured. If too dilute, acid emulsions occur, and there is great difficulty of separation.

Thus a crude whale oil containing a large amount of entangled water and albuminous matter may be best purified by using the strongest commercial sulphuric acid (C.O.V.), because the water in the oil dilutes this. The same treatment applied to another oil containing less water and less albuminous matter would discolour it, and the acid would have to be diluted with say an equal bulk of water before adding to the oil, in order to obtain the best results. The *temperature* to which the oil must be raised before adding the acid also differs for the different oils. If the temperature is *too high* the oil itself is attacked, and discoloration ensues. If the temperature is too low the albuminous matters are not effectively charred. The temperature of the oil is always below 100° C. Hence the procedure adopted in practice is to heat the oil in the tank to the proper temperature by means of the closed coil. The acid is diluted in a separate tank to the suitable concentration for the oil treated, and is then run into the oil in a thin stream while the latter is agitated by the air blast.

This operation takes from thirty to sixty minutes. As a rule two acid tanks are provided for each oil vat; so that the acid can be preparing for use in the first tank, while the second acid tank is being used for running the measured amount of acid into the oil.

The acid layer at the bottom of the oil ("foots") is run off after twelve to twenty-four hours' standing, and the clear oil washed with water or boiled up in another vessel with steam and allowed to settle, and the acid aqueous layer again run off below.

This is repeated until the oil is free enough from sulphuric acid.

The sulphuric acid treatment is not suitable for oils which are to be used for edible purposes, because this process increases the amount of free fatty acid contained in the oil, and gives them a rancid flavour. For the same reason it is unsuitable for lubricating oils, as free fatty or mineral acids will corrode the bearings of machinery, and getting into the boiler, would damage it.

It is, however, widely applied to oils where the acid content does not matter. For example, where the oils have to undergo the "Twitchell" deglycerination process.

Bleaching with Chemicals.—Actual bleaching with chemicals is only resorted to in the case of inferior or very dark oils and fats. Bleaching by means of oxygen in a nascent state is usually effected by adding manganese dioxide or sodium bichromate and sulphuric acid:—

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O$$

$$Na_2Cr_2O_7 + 4H_2SO_4 = Cr_2(SO_4)_3 + Na_2SO_4 + 4H_2O + 3O$$

Sometimes bleaching powder or sodium bichromate, together with hydrochloric acid, is used, when chlorine is evolved, thus:—

$$Ca(ClO)_2 + 4HCl = CaCl_2 + 2H_2O + 4Cl$$

$$NaCr_2O_7 + 14HCl = 2CrCl_3 + 2NaCl + 7H_2O + 6Cl.$$

The chlorine then liberates nascent oxygen, thus:—

$$Cl_2 + H_2O = 2HCl + O$$

No general rule can be given as to the best process to employ in a given case, thus *tallow* is usually bleached with manganese dioxide and sulphuric acid, and *palm oil* with bichromate and hydrochloric acid. The quantity of chemicals employed must be as small as possible, the time of interaction as short as possible, and the temperature as low as is compatible with efficiency. The glycerides may be seriously damaged if such conditions are not rigorously observed.

It will be sufficient if we describe the Hydrochloric Acid Bichromate Oxidation Process. The melted oil or fat at a temperature of about 38° C. to 55° C. is pumped into a lead-lined chemical treatment tank, compressed air is blown through it in order to thoroughly mix the contents, while the requisite amount of bichromate solution (1 bichromate : 4 water by weight) is run in. Hydrochloric acid is now added. The mixing is continued for some time while the contents of the tank are simultaneously warmed by a steam coil. Finally the liquid is allowed to settle, the acid run off at the bottom, and the oil washed with water to remove acid.

The weight of bichromate used is 1¼-1½ per cent. of the oil.

The amount of hydrochloric acid used is 2½-2¾ per cent. of the oil.

When **bleaching powder** is used it must be fresh and dry, otherwise it is largely ineffective.

The requisite quantity of bleaching powder (say 0.1-0.2 of the weight of the oil) is dissolved in as little water as possible and the concentrated solution thoroughly mixed with the oil, which has previously been heated to 50° C. to 75° C.

While the agitation is proceeding the necessary amount of hydrochloric acid (0.3-0.6 per cent. on the weight of the oil) is run in and the agitation continued for fifteen minutes. The charge is then allowed to settle, and the acid liquor run off below.

Within recent years a new class of bleaching agents has been introduced into technical practice. These are the **persalts** and **peroxides.**

The **persalts** are obtained by electrolysing the corresponding normal hydrogen salts, thus:—

$$\underset{\substack{\text{Potassium hydrogen}\\ \text{sulphate.}}}{2KHSO_4} + O = H_2O + \underset{\substack{\text{Potassium}\\ \text{persulphate.}}}{2KSO_4}$$

The nascent oxygen liberated at the anode causes the oxidising action.

The chief technical persalts are **ammonium** and **potassium persulphates**, the **perborates** and **percarbonates**. The reader will find a full account of the manufacture and properties of these bodies in Martin's "Industrial Chemistry: Inorganic," Vol. II.

All the persalts liberate nascent oxygen when heated, thus:—

$$\underset{\substack{\text{Potassium}\\ \text{persulphate.}}}{2KSO_4} + H_2O = \underset{\substack{\text{Potassium}\\ \text{hydrogen}\\ \text{sulphate.}}}{2KHSO_4} + O$$

Consequently they form powerful bleaching agents for oils and soaps (in which they are soluble). Unfortunately they are expensive in use (see German Patents, 200,684 and 205,067).

The **peroxides** are also powerful bleaching agents. The most widely employed is hydrogen peroxide, H_2O_2. **Sodium peroxide**, Na_2O_2, however, is also widely used, and reacts with water, thus:—

$$\underset{\text{Sodium peroxide.}}{Na_2O_2} + H_2O = \underset{\text{Sodium hydroxide.}}{2NaOH} + O$$

Unfortunately it is dangerous to use with some kinds of organic matter, as it can set them on fire and cause explosions.

Sodium peroxide is used technically for bleaching foots and other badly coloured oils. A solution in cold water is made and the oil agitated with it. Much foaming occurs but the treatment is effective.

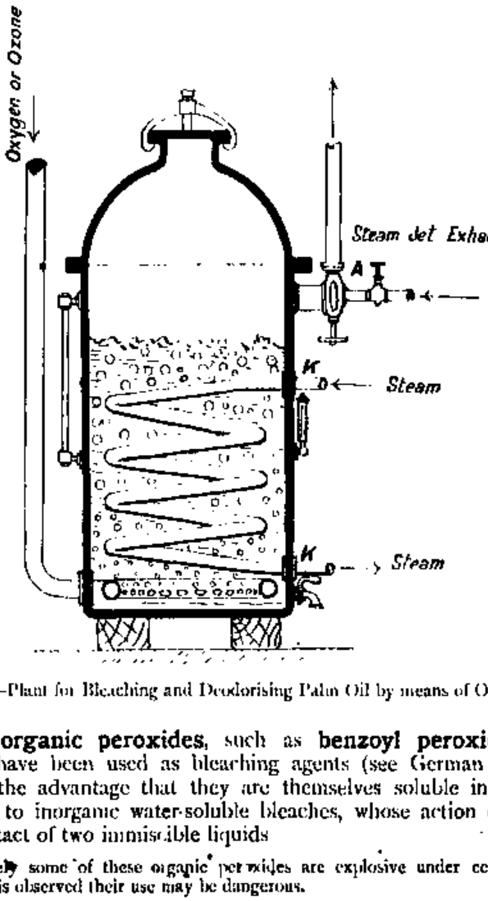


FIG. 55.—Plant for Bleaching and Deodorising Palm Oil by means of Oxygen or Ozone.

Various **organic peroxides**, such as **benzoyl peroxide** and **acetone peroxide**, have been used as bleaching agents (see German Patent, 214,937). They have the advantage that they are themselves soluble in the oils, and so are superior to inorganic water-soluble bleaches, whose action depends upon the physical contact of two immiscible liquids

Unfortunately some of these organic peroxides are explosive under certain conditions, and unless caution is observed their use may be dangerous.

Palm Oil is now bleached on quite a large scale by means of air, oxygen, and recently by **ozone**. An apparatus for bleaching palm oil by atmospheric oxygen is represented in Fig. 55. A closed vessel is fitted at A with a steam jet exhauster and a copper heating coil K K. At the bottom of the vessel is an annular air-distributing pipe with a large number of small holes connected to an inlet pipe carrying compressed air, oxygen, or ozonised oxygen.

The palm oil, which has been previously liquefied, and allowed to stand so that the water and dirt may settle to the bottom, is run into the iron vessel, heated by the steam coil to 100° C., and air is blown through. The oxygen removes most of the colouring matter, and as in this process no strong chemicals are used, the natural properties of the oil are not affected. The process may take two hours. Rank fish oils are deodorised and decolorised by this process. Sometimes, instead of air, steam at a temperature of 110° C. is driven through the oil, ten hours' steaming being sufficient to deodorise 4 tons of oil. Another method of bleaching palm oil (and which yields good results with almost all other kinds of oils) is this:—Melt, say, 100 parts of palm oil in a boiler, and when liquid add a solution of bleaching powder, made by dissolving 7 parts by weight of the powder in water for every 84 parts by weight of oil; mix intimately, cool, and cut the hardened mass into small pieces, and leave exposed to the air for a few weeks. Next place the fat in a boiler lined with lead, add a 5 per cent. solution of sulphuric acid, equivalent in total amount to the chloride of lime, heat, separate the oil from the acid, wash, and allow to solidify.

Bone Fat is often bleached as follows: Place the fat (which must be free from gelatine and calcium phosphate) in an iron pan, add an equal weight of brine of 14°-15° Bé., boil for three hours, allow to stand twelve hours, draw off the fat into a wooden vessel, and treat with a mixture of 2 parts potassium bichromate dissolved in boiling water, and 8 parts of hydrochloric acid (22° Bé.). This quantity is sufficient for 400 parts of fat. Leave the mass standing, stirring at intervals, when decoloration proceeds gradually. When complete, wash the fat with hot water.

Linseed Oil may be refined by placing 236 gallons into a copper boiler, adding 6 lbs. of oil of vitriol, and stirring together for three hours. Next add 6 lbs. of fuller's earth mixed with 14 lbs. of hot lime, stir three hours, run off the oil into a copper vessel containing an equal volume of water, boil three hours, draw the fire, and when the oil is cold, run off the water and let the mixture settle for some weeks. It is frequently decolorised by a 30 per cent. solution of $FeSO_4$ or with KOH, followed by $K_2Cr_2O_7$ and HCl. Other ways used are:—

1. *Sun Bleaching*, employed for the most expensive varieties of artists' oil. The oil is exposed to sunlight in shallow trays under glass.

2. *By Hydrogen Peroxide.*—Shake the oil in a glass bottle with a 5 per cent. solution of hydrogen peroxide, and allow to stand for some days, shaking occasionally. The oil clarifies and is poured off from the water at the bottom.

3. *By Potassium Permanganate* (suitable also for poppy oil).—Place 25,000 parts of oil in a large glass balloon, add a solution of 50 parts of potassium permanganate in 1,250 of water, stir well, allow to stand twenty-four hours at a gentle warmth, then add 75 parts by weight of powdered sodium sulphite, agitate well, add 100 parts of hydrochloric acid, again agitate, and allow to stand until decolorisation takes place. Wash the oil with water rendered milky with chalk powder until free from acid, and finally separate the water, and filter off the oil through anhydrous sodium sulphate.

Bleaching of linseed oil with chloride of lime and hydrochloric acid, or calcium bichromate and sulphuric acid, is sometimes employed, but the operation requires great care and is sometimes dangerous.

Decolorisation with Fuller's Earth, Animal Charcoal, etc.—Animal charcoal is by far the best decolorising (and deodorising) agent known, yet on account of its cost it can only be employed for edible oils and fats. More usually fuller's earth or powdered kaolin is used, being less expensive than charcoal. The oil is treated with the decolorising powder in a special mixer. The apparatus shown in Fig. 56, p. 91, is that manufactured by Rose, Downs, & Thompson at Hull. It consists of a steam-jacketed cylindrical steel tank, with a contracted neck at the top, and provided with a powerful stirring apparatus for rapidly mixing the fuller's earth with the oil. The tank is filled to the underneath part of the neck with the oil or fat to be treated (which has been previously heated to 40°-60° C.), and 3-5 per cent. of fuller's earth (the exact quantity depending upon the amount of colour to be removed) rapidly stirred in. The earth should be in the form of a perfectly dry powder. It is a silicate of aluminium.

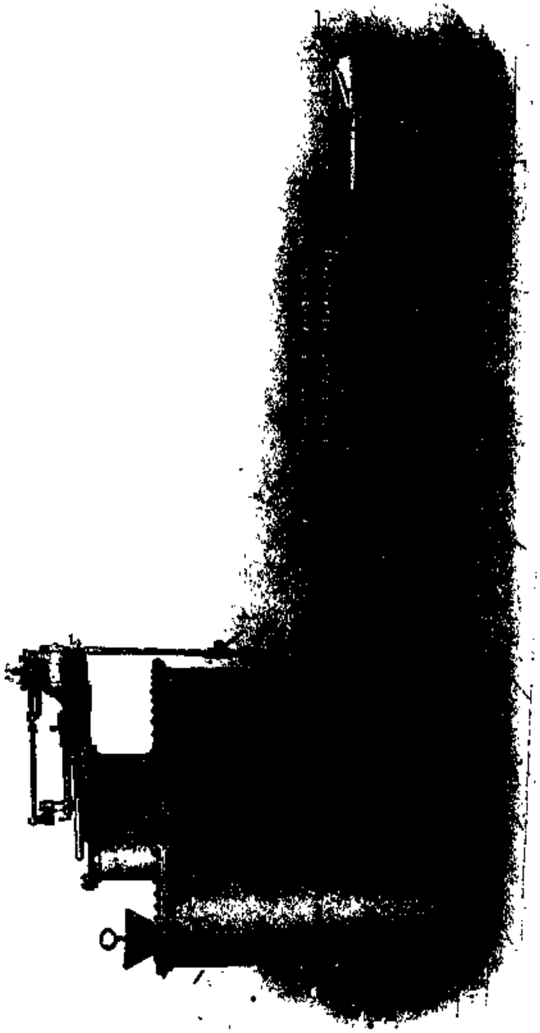


Fig. 56.—Fuller's Earth Plant. For treating lard, cotton-seed oil, coco-nut oil, ground-nut oil, etc.
(Rose, Downs, & Thompson, Hull.)

Oils and lard, which are to be used as food, must not be left in contact with the fuller's earth for more than fifteen minutes after mixing or they begin to acquire an earthy flavour. Consequently the materials must be separated as rapidly as possible after they have been stirred round for the right time.

The oil or lard is rapidly pumped away through the filter press, which retains the fuller's earth, the oil passing on through the filter cloths. Finally, steam is blown through the press so as to free the cakes from oil. When the press is opened the earth falls out as a powder upon the floor, little oil being left in it. When dealing with fats or waxes which are solid at ordinary temperatures (*e.g.*, tallow, lard, paraffin wax) the filters are steam-jacketed so that their contents can be maintained at any temperature necessary to prevent the solidification of the fat in the presses.

In works where fats are decolorised by fuller's earth, in time great mounds of this waste earth collect, and it becomes an industrial problem of some interest to extract the fat contained therein in an economical manner. A considerable amount of research work to this end has been carried out in the author's laboratory. It was found that fuller's earth freshly separated from lard refineries contained about 12 per cent. of a good extractable fat. Fuller's earth which has been used for decolorisation, and has stood exposed to the air for years, contains considerably less than this. Thus, samples 17 years old were found to contain only 3.35 per cent. of fat; samples 10 years old contained 5.4 per cent.; samples 6 years old contained 8.2 per cent.; while samples 1 year or under contained 12 per cent. fat.

Messrs Scott & Son, of London, supply plant for recovering this fat by extracting with volatile solvents. In the author's opinion it is doubtful whether it is profitable to work with less than a 10 per cent. fat content of fuller's earth. The fuller's earth is left in a moist, clay-like condition. It has been suggested that this waste residue might be profitably employed for the manufacture of disinfecting powders, boiler composition with a suitable fibre content, cement making, etc. It seldom seems to pay for using again for decolorisation of fat (on account of the cheapness of the material), but no doubt this is an industrial possibility.

The precise manner in which fuller's earth or charcoal acts is not yet understood.

Action of Cold on Oils, Demargination of Oils.—Albuminous substances are less soluble in cold than in hot oils, and so a partial purification of oils may be effected by cooling. See English Patent, 10,326, 1905 (Buchanan), and German Patent, 163,056 (Megemann).

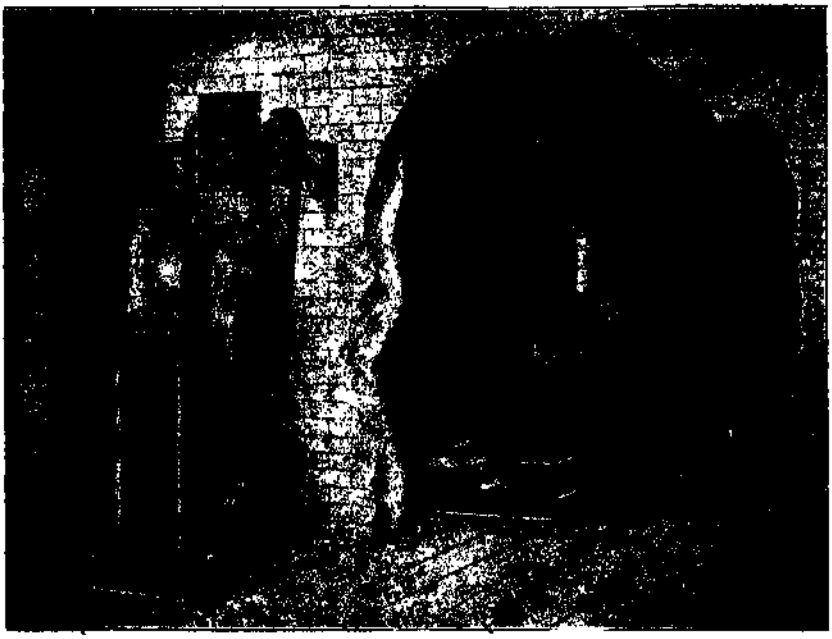


FIG. 57.—Oil Cooling and Filtering Plant, for the separation of stearin and olein.

(Rose, Downs, & Thompson, of Hull, England.)

Many of the vegetable oils (such as cotton-seed, arachis, fish, and some sorts of olive oil) deposit a crystalline mass of "stearin" on standing. It is very important that edible oils should not solidify at temperatures near the freezing point. Also lubricating oils must necessarily remain liquid at low temperatures, an oil still fluid at -15° C. being demanded for railways in the United States. Such oils are known as "Winter Oils."

Hence many natural oils must be "demarginated" before they can be placed on the market. Originally the process consisted in simply storing the oil in large vessels through the winter, when the "stearin" separated out as a white solid mass at the bottom. The supernatant oil, when drawn off, formed the "winter oil." This process is still used for arachis oil, but in other cases the cooling is artificially carried out, and the stearin removed by forcing the oil through a filter press.

Fig. 57 shows an oil-cooling and filtering plant designed by Rose, Downs, & Thompson, of Hull. The oil is placed in the tank C, which is provided with agitators and a cooling coil. The cooling effect is produced by allowing anhydrous ammonia, condensed to a liquid by the pump B, to expand through the cooling coil in the tank C. Here the liquid suddenly expands into a gas, producing intense cold in so doing. The oil, under the influence of this cold, and aided by a vigorous mechanical stirring, deposits its stearin in the solid form at the bottom of the tank. The ammonia now issuing as a gas from the cooling coil is recondensed to a liquid by the pump B, the compression being carried out in the tank C, filled with cold water, which effectively carries away the heat generated in the operation. The process is continued until the oil is reduced to the temperature at which it is desired to remove the stearin. When this point is reached the oil is drawn off and pumped through the filter press D, which removes any suspended stearin crystals.

Oil which has been treated in this way will always remain clear and bright at any temperature above that at which the stearin has been removed.

The separated stearin is a valuable product, being largely used for making margarine, margarine cheese, lard substitute, etc., etc.

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CHAPTER IX

The Hardening of Fats. The Hydrogenation of Fats

CHAPTER IX

THE HARDENING OF FATS. THE HYDROGENATION OF FATS

LITERATURE

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OFFERDAHL.—*Ber. Deutsch. Pharm. Ges.*, 1913, **23**, 558.
T. W. A. SHAW.—*Journ. Soc. Chem. Ind.*, 1914, **33**, 771.
HENDERSON.—"Catalysis in Industrial Chemistry," London, 1919.
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The following important patents should also be consulted:—

English Patents, 1,515, 1903; 2,520 and 13,042, 1907; 9,112, 1908; 7,726, 3,752, 29,612, and 30,282, 1910; 5,188, 13,519, 15,439, 25,326, and 15,440, 1911; 72, 4,702, 5,773, 18,282, 18,310, 18,996, 18,998, 22,092, 23,377, 23,643, 24,084, 27,718, 28,754, 28,981, 1912; 4,144, 10,204, 11,542, 11,543, 13,382, 16,283, 16,782, 18,350, 1913; 2,306, 2,307, 3,344, 3,865, 4,665, 5,967, 15,668, 16,600, 1914; 109,993, 1917; 129,461, 1918.

German Patents.—211,669, 1907; 221,890, 1910; 236,488, 1911; 260,885 and 256,500, 1913.

French Patents.—450,703, 1912; 458,445, 1913.

U.S.A. Patents.—902,177, 1908; 1,004,034, 1911; 1,004,035, 1911; 1,040,531, 1,040,532, and 1,043,580, 1912; 1,059,720, 1,058,738, 1,060,673, 1913.

OLEIC acid is an unsaturated acid only differing from stearic acid by the absence of two hydrogen atoms. Several processes have been proposed for making **Oleic Acid** take up these two hydrogen atoms and become stearic acid, according to the equation:—

$$\underset{\text{Oleic acid.}}{C_{17}H_{33}COOH} + \underset{\text{Hydrogen gas.}}{H_2} = \underset{\text{Stearic acid.}}{C_{17}H_{35}COOH}$$

Thus fuming hydriodic acid reduces oleic acid to stearic acid; so does heating with iodine; other attempts to reduce oleic acid to stearic acid have also been successful. For details of these and other processes the reader isr eferred to the *Journal of Chemical Industry*, 1908, vol. 27, p. 489.

Recently it has been shown that when **Oleic Acid** is treated with nickel powder in the presence of hydrogen, it takes up hydrogen and gives an almost theoretical yield of hard stearic acid.

Moreover, this latter action is of general importance. Not only does oleic acid but also liquid *unsaturated fats* take up hydrogen under these conditions and become converted into hard substances. Thus the liquid glyceride, triolein, is converted into solid tristearin:—

$$C_3H_5(OOC.C_{17}H_{33})_3 + 3H_2 = C_3H_5(OOC.C_{17}H_{35})_3.$$

Sabatier and Maihle (*Ann. Chim. Phys.*, 1909, [8], **16**, 73) showed that oleic and elaidic acids, when treated with hydrogen in the presence of *reduced* nickel at 280°-300° C., yielded stearic acid. The nickel, technically prepared by reducing nickel carbonate *in situ*, is thrown into the heated fat and H gas is passed through.

The first patents referred to the passage of hydrogen gas through *the vapours of* fatty substances. Such processes were of little use in the case of glycerides, as they are decomposed when vaporised.

The fundamental patent was taken out by Norman (English Patent, 1,515, 1903), which described the hydrogenation of oils in a liquid condition, by merely passing a current of hydrogen into the oil, heated to a suitable temperature, and containing a finely divided metal as catalyst.

This patent is fundamental in character since it precluded all other manufacturers from hydrogenating oils in the liquid condition. In 1913, however, it was declared to be invalid owing to the meagre information given in the patent.

Recent work has been principally directed towards the preparation of the catalytic nickel in a suitable state, the best proportion of catalyst to use, the best temperature of hydrogenation, the proper refining of the fatty body, the application of continuous mechanical agitation, the purification of the hydrogen.

For details of these the reader must consult the patent literature above referred to. Published details are meagre. Crossley (*loc. cit.*) gives details for rape oil, whale oil, etc., which were published in the lawsuit of Joseph Crosfield & Sons, Ltd., *v.* Technico-Chemical Laboratories, Ltd.

The method was invented by Sabatier and Senderen. The reader will find a résumé of their researches in the *Annales de Chimie et de Physique*, 1905, [8], **4**, 319; 1909, [8], **16**, 70. See also Sabatier, *Ber.*, 1911, **44**, 1984; Sabatier, "La Catalyse."

An excellent account is also given by Crossley, *The Pharmaceutical Journal and Pharmacist*, 1914, **92**, pp. 604, 637, 676. See also C. Ellis, *J.S.C.I.*, 1912, **31**, 1155; also his book, "Hydrogenation of Oils," 1914; T. Shaw, *J.S.C.I.*, 1914, **33**, 771.

Theoretical.—At constant temperature and pressure the velocity of hydrogenation of an oil is given by the equation:—

$$V = K.C_1C_2.$$

Where V is the velocity of the reaction, K the constant of reaction, C_1 is the active mass of the oil, and C_2 the active mass of the hydrogen.

Consequently, in designing a plant for the hydrogenation of oil it is essential that the product C_1C_2 should be as large as possible. In other words, the product of the number of pounds weight of hydrogen per minute driven against the oil into number of pounds of oil it meets per minute must be as large as possible.

Hence the hydrogen should be highly compressed, as in this way a larger weight is concentrated in a given volume. Also the speed with which the oil and hydrogen circulate in the system in a counter-current direction should be as great as possible. Hence the pumps should be powerful, and it is theoretically a mistake to depend upon gravitation and ordinary pressures for the flow of gas and oil. The great practical advantage of the latter arrangement is ease of working and simplicity of plant.

It is also well known that an increase of pressure favours the formation of products possessing a smaller volume than the original components. Since the hydrogenated oils occupy less volume than the original hydrogen and oil mixture, on this ground also (see below) it is advisable to use high pressures and powerful pumps.

The reaction is *mono-molecular*. Fokin (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 276) has shown that the saturation with hydrogen of a double bond at constant temperature and pressure follows the ordinary mono-molecular formula:—

$$K = \frac{1}{t} \log \frac{a}{a - x}.$$

Where *a* represents the total volume of hydrogen absorbable by the unsaturated oil, and *x* the volume of hydrogen actually absorbed after the time *t*.

The reaction starts rapidly, but slows down as saturation is attained, following in this the ordinary mono-molecular formula:—

$$\frac{dx}{dt} = K(a - x).$$

The saturation of an oil with hydrogen is *exothermic*, *i.e.*, attended with the evolution of heat. Maxted ("Catalytic Hydrogenation and Reduction," pp. 95 and 97) states that, in the course of a two hours' run, a charge of oil will have spontaneously increased its temperature from 140° to 185° C.

If Q be the heat of reaction and K the equilibrium constant, K is dependent upon the temperature according to van't Hoff's equation :—

$$\frac{d \log K}{dT} = \frac{Q}{RT^2}$$

Consequently K tends to diminish with rise of temperature, and for this reason it is advisable to carry out the hydrogenation at as low as possible a temperature compatible with a sufficient practical velocity of reaction. The formation of bodies whose production is attended with the evolution of heat (*i.e.*, exothermic bodies) is checked by rise of temperature.

Practical Conditions of Success

It has been found that the main conditions for success in the hydrogenation of oils in the liquid condition are :—

1. **Exact Control of the Temperature**, *e.g.*, the reduction of the oil with nickel must take place at as low a temperature as possible—say 140°-180° C.—in order to avoid decomposing the oil and giving it a bad taste and colour. Again the nickel must be reduced at a low temperature (see below).

2. **The Purity of the Reacting Bodies**, *e.g.*, the *fats* should be purified by removing free fatty acids (not more than 1 per cent. free fatty acid should be present) and moisture, sulphur compounds, etc.

The *nickel* must be pure (see below). The *hydrogen* must be extremely pure if good results are to be attained. The purer the hydrogen the more rapid the reduction. Sulphur compounds, arsenic, water, carbon monoxide in the hydrogen all diminish its activity in the presence of nickel.

3. **The Exclusion of "Catalytic Poisons,"** *i.e.*, substances which destroy the hydrogenating action of the nickel catalyst.

Chlorine, sulphur (as sulphide), phosphorus, and arsenic are the worst of these catalytic poisons. Oxygen and water and carbon monoxide also affect injuriously the activity of the nickel.

4. **The Fine State of Division of the Catalyst.**—The more finely divided the catalyst the more rapid the action.

5. **The Pressure of the Hydrogen Gas.**—Several processes exist in which the hydrogenation takes place under ordinary atmospheric pressure, and it is true that if the catalyst is sufficiently active an almost instantaneous conversion of the oil is possible. Nevertheless, in general the higher the pressure employed the more rapid and effective the hydrogenation ; four atmospheres is a good working pressure. Bergius (*Zeit. Angew. Chem.*, 1914, **27**, 522) actually showed that the hydrogenation of oil can be effected without catalytic aid by the use of high temperatures and very high pressures.

In general a catalyst only acts in accelerating a chemical action which takes place of itself at a sufficiently high temperature and pressure.

It is a well-known law of physical chemistry that an increase of pressure favours the production of reaction products, having a smaller volume than the products we start with. As the hydrogenation of fats is attended with the absorption of hydrogen so that the resulting hydrogenated oil occupies a smaller volume than the hydrogen and oil we start with, this result of Bergius is to be expected on theoretical grounds.

6. **An Adequate Intermingling and Mixing of the Hydrogen and the Oil.**—It is obviously essential to mix the hydrogen and oil effectively by means of stirring gear or other devices.

This need of mixing has probably been exaggerated in the patent literature. The hydrogen can only act by solution in the oil, and the nickel, once wetted by the oil, cannot come into contact with the gas except by solution ; so that all that is needed is a gentle mixing of the contents. Very rapid diffusion also aids the action. Hence the large number of patents which describe complicated devices for bringing hydrogen and oil into intimate contact by violent agitation, or "atomisation," are probably introducing needless elaboration into the plant necessary for successful treatment of oil with hydrogen.

It has been shown that the activity of the nickel catalyst depends upon:—

1. **The Purity of the Nickel.**—For example, in preparing the nickel from nickel sulphate by precipitating as nickel carbonate by means of sodium carbonate, and then reducing the latter in hydrogen, it is absolutely essential to wash the nickel carbonate after precipitation until it is quite free from all traces of sulphate. Sulphur compounds affect the activity of the catalyst very badly, and consequently some authorities prefer to work with nickel nitrate, precipitating it as nickel hydroxide by caustic soda, washing, drying, and reducing.

2. **The Temperature of Reduction.**—It is necessary for the nickel to be extremely finely divided so as to be in a pyrophoric condition, *i.e.*, the metal spontaneously inflames on contact with air or oxygen. This condition is only attained by carrying out the reduction with hydrogen at as low a temperature as possible. Thus nickel oxide begins to reduce at 200° C. Reduction is incomplete below 270° C. The usual temperature employed is 300°-320° C. Too high a temperature of reduction (say 400° C.) converts the nickel into an almost inactive modification. Nickel carbonate is said to be sufficiently reduced at 230° C. (see Fuch's patent, English Patent 11,542, 1913), *i.e.*, a lower temperature than is necessary with the oxide.

Organic salts of nickel can be reduced at still lower temperatures (see Wimmer-Wiggins Patents; see English Patents, 25,326, 1911; 4,144, 1913).

3. **Protection from Oxidation.**—The finely divided nickel after reduction must not be allowed to come into contact with air, otherwise it oxidises and becomes inactive. It is therefore either kept in an atmosphere of hydrogen until use, or else dropped into oil immediately after reduction, and kept in that way. In some processes the nickel carbonate is reduced in the oil itself. (See below.)

4. **Use of Nickel Carbonyl.**—Shukoff (German Patent, 241,823, of 18th January 1910) employs an entirely different method of preparing the nickel catalyst. He passes *nickel carbonyl* (obtained by action of carbon monoxide on reduced nickel at a low temperature) into oil heated to 200° C. The nickel carbonyl is decomposed and metallic nickel is set free. Lessing's process (see English Patent, 18,998, of 1912) uses this fact for his process of hydrogenation.

5. **Use of Carriers for Nickel.**—In order to increase the catalytic effect of a given quantity of nickel a large number of patents have been taken out for the use of carriers. Thus, pumice, kieselguhr, asbestos, and other porous bodies are impregnated with nickel salt, and the whole reduced with hydrogen.

Modern practice, however, has tended to diminish the use of these carriers. They aid filtering off the nickel.

Many proposals have been put forward for increasing the *activity* of the hydrogen used in reducing the fat.

Thus Fuch (English Patent, 11,543, 1913) suggests:—

1. Heating the hydrogen to 200°-250° C.—a higher temperature than that of the fat to be reduced.
2. Dissociating the hydrogen into atoms by treating it with chemically active rays.
3. Passing the heated hydrogen over a catalyst such as spongy platinum or freshly prepared nickel, which appears also to increase the chemical activity of the hydrogen.

For use of electrical discharges, chemically active rays, etc., in increasing the activity of the reacting materials (see Utescher, British Patent, 20,061, 1912), where the use of mercury vapour lamps is suggested. In this connection see also *Seifen Ztg.*, 1913, p. 851; F. Gruner, French Patent, 453,664, 1913. In the latter patent oils and fats are subjected to the action of an electric current of very high tension and frequency. 50,000 to 100,000 volts are mentioned. Farmer and Parker (*Journ. Amer. Chem. Soc.* (1913), p. 1524) describe experiments on the effect of ultraviolet light on colloidal platinum.

Use of other Metals than Nickel.—In addition to nickel and its compounds, colloidal platinum (Fokin, Willstatter), and palladium (Paul), copper and iron may be used. Palladium has been used industrially in amounts as small as $\frac{1}{5000}$ to $\frac{1}{10000}$ of the amount of fat (see Paul and Skita, German Patent, 230,724; *Ver. Chem. Werke A.G.*, German Patent, 236,488, 1919; British Patent, 18,642, 1911; palladium chloride (with rubber or gelatine as protecting colloid) is used. Reduction with platinum or palladium takes place at a lower temperature than when nickel is used.

Supply of Hydrogen for Hydrogenating Fats.—One ton of oleic acid requires about 79,000 litres (2,800 cub. ft.) of hydrogen. One ton of Triolein (*e.g.*, the glycerine of oleic acid) requires 75,900 litres (2,680 cub. ft.) of hydrogen.

The production of hydrogen for this purpose is fully described in Martin's

"Industrial Chemistry: Inorganic," Vol. I., to which the reader is referred for fuller details.

It might be mentioned here that the hydrogen is mainly prepared by the following methods:—

1. **Electrolytic.**—This method produces a very pure gas, but is too expensive to compete with the other processes except in countries like Norway, where water power is cheap, and where this process actually is the dominant method of producing hydrogen. Caustic soda solution is the usual electrolyte.

2. **Iron Sponge Steam Process.**—Oxide of iron is reduced by means of water gas carefully purified from sulphur compounds. Steam is then passed over the heated reduced metal, yielding the oxide and hydrogen. The oxide is again reduced by water gas. (See below.)

Lane's Plant is one of the best-known and successful plants for working this process. **Maxted** (Gas Developments, Ltd., Walsall, Birmingham) has modified this process so as to produce a gas as pure as electrolytic hydrogen but at less cost. (See below.)

3. **The Harger-Terry Process** (see British Patent, 6,007, 1917) consists of impregnating impure hydrogen with the proper amount of electrolytic hydrogen and oxygen, and passing the resulting mixture over a suitable heated catalyst. The carbon monoxide, sulphur, and phosphorous compounds are oxidised, and absorbed by lime or alkali. The resulting hydrogen is exceedingly pure.

The Linde-Caro Process.—Water gas is liquefied and the hydrogen separated from the CO by fractional distillation. The gas used for hydrogenation consists of H = 95-97 per cent., CO = 2 per cent., rest = N. The pumping is done by a gas engine utilising the separated CO as fuel.

The hydrogen used must be free from H_2S, 0.1 per cent. being sufficient to destroy the catalytic activity of nickel.

In 1913 the Linde Co.'s plants for producing H for the hardening of fats (*Zeit. Angew. Chem.*, 1913, **26**, III. 814; see also Vol. II., "Industrial Hydrogen,") yielded enough H to harden 100,000 tons of fat.

Industrial Processes for Hardening Fat.—A very large number of processes have been described in the patent literature, but very few have proved technical successes. The reason is that considerable technical difficulties occur, especially in working on the large scale, and many of the patents describe processes in which these difficulties have proved insuperable.

Description of Processes.—Hydrogenation processes involving the use of nickel may be divided into three classes:—

(1) Dry processes.
(2) Wet processes.
(3) Gaseous processes.

(1) **Dry Processes.**—In these the catalyst is produced by treating the oxide of nickel in a dry state with hydrogen gas at a temperature of about 300° C.

The reduction of the nickel is attended with many difficulties. In the first place, in the furnace a stirring apparatus is required in order to mix the nickel oxide thoroughly with the hydrogen. Hence the employment of rotary drums, stirring autoclaves, etc., the heating of which presents several difficulties. Again the sensitiveness of the catalyst depends very largely upon the temperature.

If the temperature is too high (400° C.), the nickel will pass from the catalytically active black form into the inactive grey modification. The lower the temperature of reduction the more active the nickel. But if the temperature of reduction is too low (*i.e.*, below 250° C.) the reduction of the nickel is imperfect.

Consequently the temperature of reduction has to be very carefully regulated, and this is a difficult matter to effectively control.

The reduced nickel, also, is very chemically active, and if not protected from oxidation, will lose its catalytic power. Also the opening of the reducing apparatus may be dangerous, as the reduced nickel will take fire in air, and if hydrogen is present in sufficient quantity this may cause an explosion—as has actually occurred in practice. Hence before opening the apparatus the hydrogen must be swept out by an inert gas like carbon dioxide.

The catalyst, when made, must also be employed under exactly defined conditions.

Some workers consider that nickel reduced in the dry state is too compact to be used as such, and so they place it on special "supports," such as clay, asbestos, etc. These materials obviously add to the difficulty of regenerating the nickel, and it has been stated that they may give to the fat an earthy taste and bad colour. Moreover, much fat is absorbed in their pores, the recovery of which is difficult.

Finally, the catalyst is mixed with the mass of oil to be hardened, and while actively agitated hydrogen gas, under a pressure of 4-5 atmospheres, is heated to a suitable temperature, say 140°-250° C.

The following works have been stated to be using processes of this type:—

Process.	*Works.*
NORMANN	Germaniawerke, Emmerich. Schichtwerke, Aussig. Jurgene, Ose.
WILBUSCHEWITSCH	Lever Bros., Port Sunlight. Bremen-Bersigheimer Oelfabriken. De No Fa, Frederikstad. United Soap Works, Zwinndrecht. "Salolin," Petrograd and Nischni-Novgorod.
CARLTON ELLIS	Hydrogenated Oil Co., New York. Southern Cotton Oil Co., New Jersey and Georgia.
C. E. KAYSER	Procter Gamble Co., Cincinatti.

The following details give a rough outline of the methods employed in this process. Plant and autoclaves are sold by Lane (Ashford, Middlesex, England), and also by Maxted (Gas Developments, Ltd., Walsall, near Birmingham, England) for these processes.

Normann Processes.—The following is a brief account.

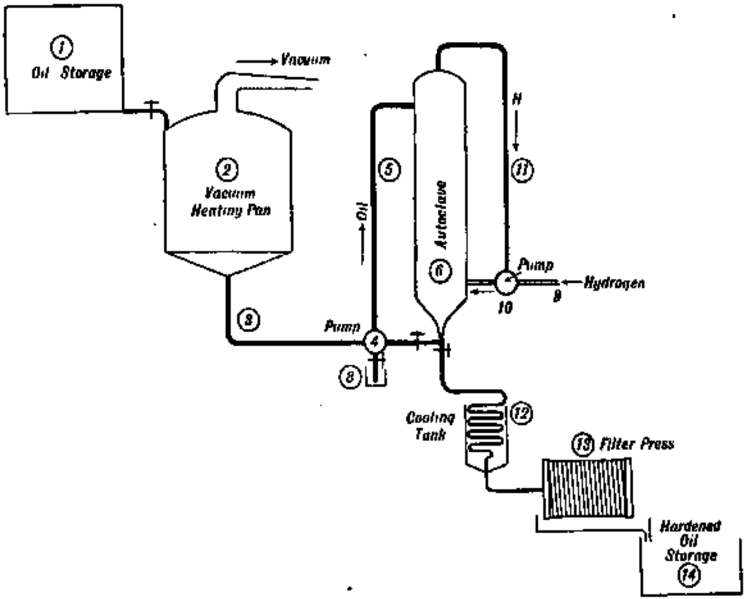


FIG. 58.—Normann Process of Fat Hardening.

The fat to be hardened must contain less than 1 per cent. of free acids, otherwise nickel soaps will be formed, and nickel will appear in the refined fat. Hence, before hardening, the fat should be refined, as this will pay in the end. The fat must be dry. For this purpose it is run from a storage tank 1 into a vacuum heating pan 2, and is there heated until water is eliminated. It is then run down the pipe 3 and forced by the pump 4 up the pipe 5 into a heated autoclave 6. This autoclave is steam-heated, and is kept at a temperature of about 140° C. The pressure inside the autoclave is about 5 or 6 atmospheres. The interior is usually fitted with baffle plates, and sometimes with stirring gear, so that the liquid in pouring down the interior of the autoclave is very intimately mixed with an ascending stream of hydrogen gas. The fat reaching the bottom of the apparatus is pumped by 4 up the pipe 5, and in again at the top of the apparatus, so that a continual circulation of the fat is produced until the degree of hardening required is attained.

The hydrogen gas is drawn into the apparatus through the pipe 9, and by means of the pump

10 it is forced into the bottom of the apparatus, and passes up the autoclave against the descending stream of liquid fat, and is intimately mixed with it. The unabsorbed hydrogen collects at the top of the apparatus and then passes down the pipe 11, and once again is injected into the apparatus by the pump 10.

As the hydrogen is absorbed fresh supplies are passed in through the tube 9.

The catalyst is supplied as follows:—Nickel carbonate (made from nickel sulphate) is placed in a furnace and calcined. It is then ignited in a stream of hydrogen gas, so that it is reduced to the state of a metal in a finely divided condition. While still hot, and in an atmosphere of hydrogen, the charge of nickel is quenched in oil contained in a receiver. The oil containing the proper charge of nickel is then pumped from the vessel 8 into the autoclave 6 through the pump 4. It thus mixes with the charge of fat, and supplies the correct amount of nickel for the charge.

The hydrogenation proceeds rapidly, and is carried on until the iodine value sinks to about 60. It is important that the fat should not be too hard for edible purposes. The melting point of such fats should always be lower than that of the human body.

The nickel is usually recovered by running the fat out of the autoclave through partial coolers 12, so as to reduce its temperature somewhat (in order to avoid damaging the filter cloths), and it is then pumped through a filter press 13, into the storage tank 14, and the finely divided nickel is recovered and either sold as such to nickel manufacturers, or else it can be worked up again into sulphate.

The hydrogenation begins at about 140° C. with pure hydrogen, and the temperature then rises somewhat (the action being exothermic) up to 180° C. The lower the temperature is kept the better the resulting fat for edible purposes.

Maxted's Oil Hardening Installation

The arrangement of a Maxted oil hardening installation, designed for the treatment of about 100 tons of oil per week, is shown diagrammatically in Fig. 59.

It may be divided broadly into two sections, one of which is devoted to the production of hydrogen, while in the second portion, namely that shown on the right of the diagram, the hardening operation itself, together with the manufacture of catalyst, is carried out. The raw material for the manufacture of hydrogen is coke, which is gasified in generators of the intermittent type shown as A and A¹.

The essential part of the process employed for the manufacture of hydrogen of the high degree of purity necessary for successful hydrogenation, consists in the substitution of a special reducing gas in place of the water gas usually employed for such purposes.

Ordinary water gas, by reason of the instability of carbon monoxide, at elevated temperatures, especially in the presence of iron oxide, readily deposits carbon according to the equation

$$2CO = CO_2 + C,$$

so that if water gas of the usual composition is used for the reduction phase of the intermittent process of hydrogen production, in which iron oxide is alternately reduced and steamed in two separate operations, the deposit of carbon thus produced remains on the contact mass and persists into the steam phase, where by the interaction of this carbon with steam according to the ordinary water gas reaction, carbon monoxide is generated and contaminates the hydrogen simultaneously produced by the action of steam on the reduced iron.

$$C + H_2O = CO + H_2.$$
$$3Fe + 4H_2O = 4H_2 + Fe_3O_4.$$

This undesirable deposition of carbon during the reduction phase, which involves the subsequent production of impure hydrogen, is avoided by taking advantage of the reversibility of the deposition reaction, $2CO \rightleftharpoons CO_2 + C$, in that for the reduction of the contact mass a gas is employed, the carbon dioxide content of which bears a ratio to the carbon monoxide present equal to or slightly in excess of the equilibrium carbon dioxide monoxide ratio for the temperature of reduction, a reducing gas of this composition being produced from coke, and freed from steam before being used for reduction.

B and B¹ are scrubbers, C and C¹ iron oxide purifiers, and D a gasholder, all for reducing gas.

The actual generation of hydrogen by the alternate reduction of iron oxide and steaming of the iron thus produced is carried out in vertical cast-iron retorts contained in the furnace shown at E, the hydrogen produced being freed from steam by means of the surface condenser F, and from the last traces of sulphur and carbon dioxide by means of an iron oxide lime purifier G. For the above size of installation a hydrogen plant capable of producing 2,500 cub. ft. of hydrogen per hour is provided, the gas being finally stored in the gasholder H. Should there be the probability of hydrogenating linseed or other highly-unsaturated oils, a hydrogen installation giving 5,000 cub. ft. per hour is necessary.

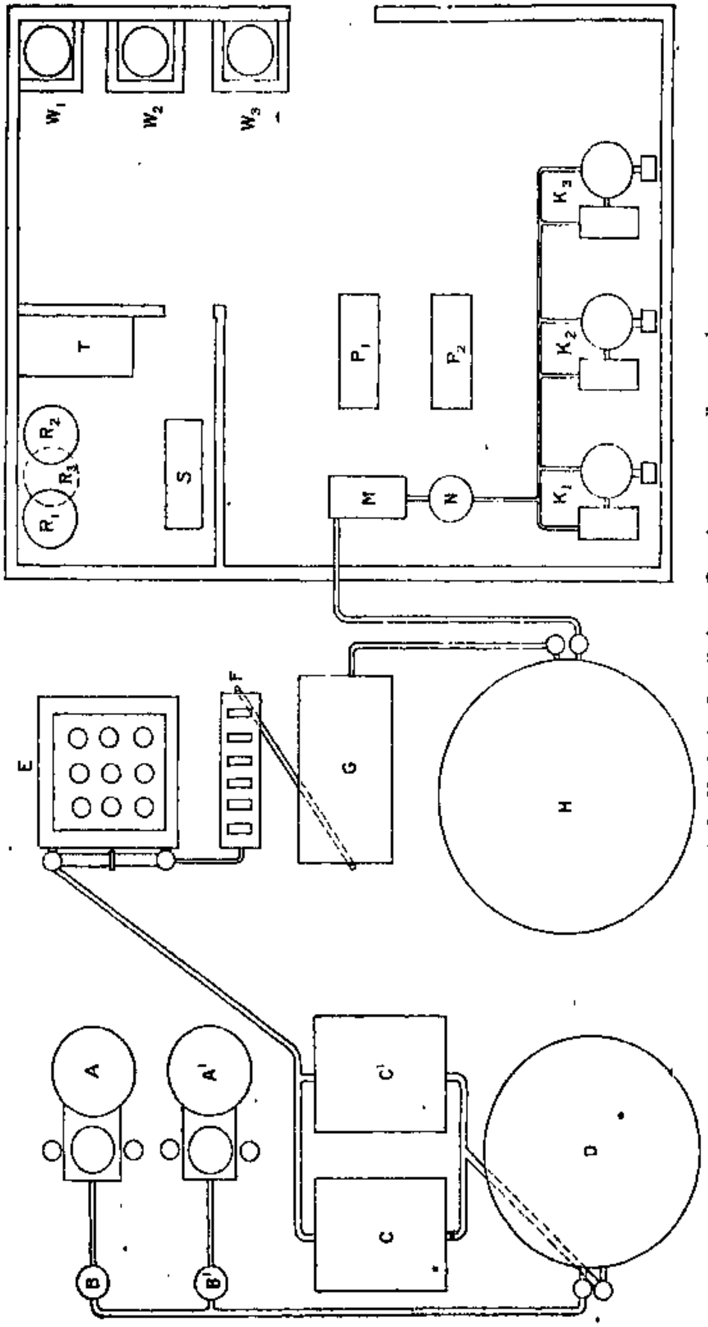
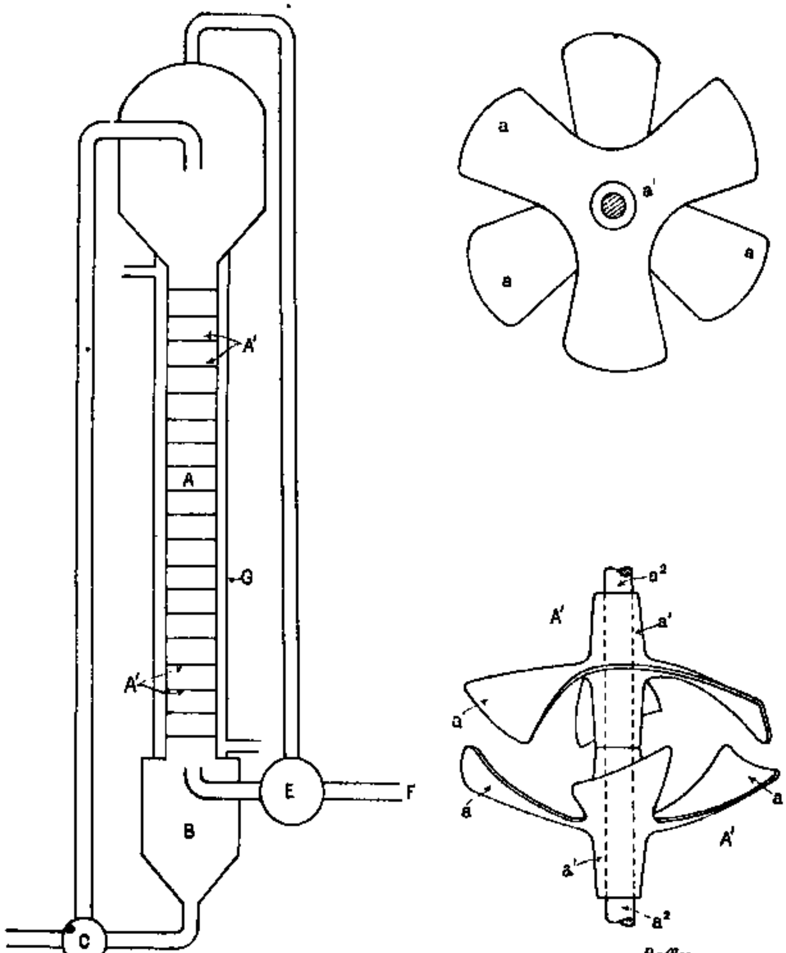


FIG. 59.—Maxted's O Hardening Installation. Capacity, 100 tons oil per week.

It is found possible to produce by the above method hydrogen possessing a purity of 99.9 per cent. and even more, constantly and without specially skilled attention. Carbon monoxide is completely eliminated, and a high degree of freedom from air and its components may, if desired (although quite small traces of entrained air are not objectionable in hydrogen employed for oil hardening), be avoided by using air-free steam for the hydrogen furnace and surface condensers in place of open scrubbers for freeing the hydrogen from steam after generation.



Baffles.

Fig. 60.—Maxted's Oil Hardening Autoclave.

The hydrogenation portion of the plant comprises, for the size of installation in question, three hardening vessels shown at K_1, K_2, and K_3, each capable of taking as its charge 1 ton of the oil to be treated.

A hardening vessel is shown in greater detail in Fig. 60. It consists of a cylindrical portion A, containing a series of special baffles, and welded to enlarged upper and lower portions. Attached to the vessel is a gas circulating pump E, by means of which hydrogen is drawn out of the top reservoir and projected at a high velocity upwards through the column A, while the oil pump C circulates oil from the bottom reservoir, and delivers it at the top of the column A.

In practice these pumps work sufficiently quickly to fill the entire vessel with an intimate mixture of hydrogen and oil, bordering on a froth, the degree of contact being to a large extent brought about by the construction of the baffles contained in the column. These are of propeller-like form, and are alternately right and left handed, in addition to being constructed in such a way as to prevent the formation of a central core either of gas or oil. The baffles are, of course, fixed, the required emulsification of oil and hydrogen being effected by the forced motion of these, in counter-current to one another, through the column. The baffles are shown on the left-hand side.

Hydrogen to compensate for that absorbed by the oil is supplied as required from the pressure reservoir N (see Fig. 59) into which hydrogen from the holder H is compressed by means of the compressor M.

The time required for the hardening of an oil varies, of course, with the nature of the material treated, and with the degree of hardness required, together with the amount of catalyst employed, and the temperature at which hardening is begun.

It is the practice in the Maxted system to keep the temperature of reaction as low as possible, with a view to avoiding deterioration in flavour of the product where this is to be used for edible purposes. The temperature at which hardening is begun is usually 135°-140° C., the proportion of nickel catalyst being from 0.5-1 per cent., according to the quality of the oil.

As an example of time required for hardening under the above conditions, a charge of refined arachis oil was hardened down to an iodine value of 54 in one hour and ten minutes for hardening to an iodine value of 27, the temperature being in the former case maintained at 140° C., while in the latter it was allowed to rise from 140°-185° C. by reaction heat.

The oil after hardening is freed from catalyst by means of the steam-heated filter presses shown in Fig. 59 at P_1 and P_2.

The remainder of the installation is concerned with the manufacture of the supply of fresh catalyst necessary for replacing that rendered inactive by continued use.

This catalyst plant consists of precipitating tanks R_1, R_2, and R_3, for the manufacture of nickel hydroxide or carbonate by the interaction of aqueous solutions of nickel sulphate and soda. The precipitate is filtered and washed by means of one filter press S, the filter cake of unreduced nickel catalyst being dried in the drying room T, and subsequently reduced to metal by means of hydrogen at a temperature of slightly more than 300° C. in the reducers W_1, W_2, and W_3.

The pyrophoric nickel thus obtained is allowed to cool in hydrogen or in an inert gas such as nitrogen, after which it is stored in oil, and introduced in this form into the hardening vessels as required.

Lane's Installation for Hardening Oil.—Mr Howard Lane, of the Laboratory, Ashford, Middlesex, England, after the perfecting of the Lane Hydrogen Process, turned his attention to the installation of fat hardening plant, and has worked out the process in detail.

Fig. 61 shows a plan of an oil hydrogenising factory designed by Mr Lane.

The installation is to deal with 2 tons of oil per hour. The oil must be purified.

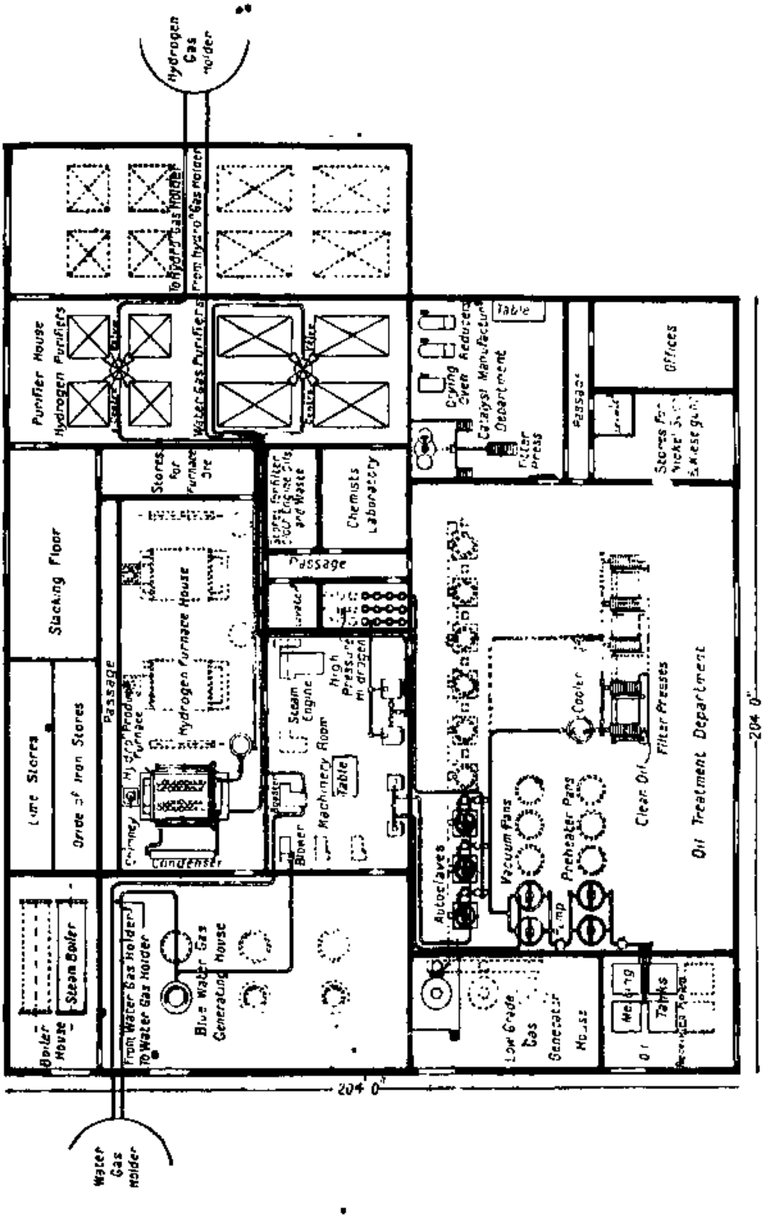
The refined oil is brought in casks to the works and emptied into tanks.

Four melting tanks are employed, being 8 ft. square by 4 deep, and provided with gratings on which to roll the casks and wire gauze to strain the oil from impurities which might choke the pumps. The melting tanks are provided with hot water coils to melt the oil and keep it liquid, and also have 3-in. iron cocks at the bottom.

From the melting tanks the oil is pumped into six vacuum drying pans, each capable of holding 1½ tons of oil. Here the oil is heated (using gas heating, not steam) under vacuum, until thoroughly dry. The final temperature of the oil is 150° C. The oil is then ready for transference to the hydrogenising autoclaves.

The **pumps** used for transferring the oil from the melting pans to the vacuum drying pans should be capable of dealing with 250 gallons of oil per minute. Also they should be in duplicate in order to avoid delays in cleaning or stoppage.

The **vacuum pans** are 5 ft. in diameter and 6½ ft. high, made of steel plates ⅜ in. thick with dished ends ½ in. thick. They are fitted with stirrers. Each pan is set in a cast-iron case lined with firebrick and provided with a gas ring burner for heating, air slide doors for access and air supply, and with a chimney 15 ft. high. The pans are fitted with the necessary test cocks, thermometers, pressure and vacuum gauges.



Plan of Oil Hydrogenising Factory on the Lane System Shafting & Doors omitted

FIG. 51.

The charge of oil which each pan takes (viz., 1½ tons) is exactly that which the hydrogenising autoclave takes.

The **vacuum pumps** for the pans and autoclaves should be in duplicate, each capable of dealing with the whole requirements of the plant. They should be capable of reducing atmospheric pressure down to that measured by a column of mercury 28 in. high.

The displacement of each pump, as measured by the stroke and diameter of its pistons operating for one minute, must not be less than 120 cub. ft. Each vacuum pump should be provided with an interceptor or collector vessel, so that moisture and impurities coming from the oil may be intercepted and condensed before passing into the mechanism of the pumps.

These interceptor vessels should have a capacity of at least 50 cub. ft., and should be internally provided with cooling coils so as to condense the hot fatty acids and water coming over from the autoclaves. The interceptor vessels should be in duplicate, with change over valves, so that one is in service while the other one is being cleaned.

It is important to exclude air from contact with the hot oil, and in order to achieve this the vacuum pans are connected with a low pressure hydrogen supply, while the valve at the bottom of the pans is connected with the hydrogenising autoclave, which is also evacuated. The oil is thus caused to flow out from the heating pans into the hydrogenising autoclave, and the space occupied by the oil is taken by hydrogen. So that from start to finish the hot oil never comes into contact with air, but is either maintained in a vacuum or in contact with an indifferent atmosphere of hydrogen gas.

As soon as the pan is empty of oil a fresh charge of oil is pumped in.

The **hydrogenising autoclaves** are six in number for a 2 ton per hour plant.

The drawings (Fig. 62A) show the construction of Lane's most recent hydrogenising autoclave, both in sectional elevation and frontal elevation. Older forms are shown in Fig. 62B.

Each autoclave is provided with a pipe and valve connection to the vacuum drying pans, a hydrogen connection pipe at the top and bottom, a vacuum connection, a pipe for the introduction of oil and catalyst, and a discharge pipe for the hardened oil.

The autoclave is heated, as indicated, by gas, a ring burner being provided around the base of the autoclave. The combustion jacket surrounding the autoclave is open at the top and lined with firebrick. Vacuum gauges, pressure gauges, test cocks, and thermometer pockets are provided. In the older form of the autoclave it was provided with a stirring shaft, worked from the top of the autoclave, and provided with beaters and shelves, as indicated in Fig. 62B. But in the most recent form this stirring shaft is worked from below, and both the propeller of the pump and the atomising shaft being driven externally as indicated in Fig. 62A by a half-crossed belt, the shaft emerging through a hydraulically packed water cooled stuffing box. The autoclave is provided with an inner casing, and at the base of the autoclave (but inside it) is a centrifugal pump worked by the rotating shaft. The oil is thus thrown out at the base of the autoclave, passes up between the inner and outer casings in virtue of its centrifugal motion, falls over the top of the inner casing on to the shelves, and falls downwards inside the casing from shelf to shelf, being struck and atomised as it falls by the beaters attached to the rotating shaft. In this way a very intimate mixture of hydrogen and oil is attained. The oil is also heated uniformly and rapidly by circulating rapidly against the heated surface of the outer casing.

In order to control the amount of the oil passing through the turbine pump a disc valve is arranged to be raised or lowered by means of a sliding sleeve passing through the boss of the propeller.

The autoclave is 4 ft. in diameter and 14 ft. high, and is made of ⅝-in. plates, and is tested to 200 lbs. pressure per square inch.

The charge is 1½ tons of oil.

The autoclave is charged as follows:—

The autoclave is placed under a vacuum after previously filling with hydrogen, and the oil inlet is then opened and the oil rushes in from the vacuum drying pans until the bulk of the oil has entered, but a little oil is purposely held back. Next the atomiser pump and shaft are set into action and the charge of catalyst introduced. The remainder of the oil is then delivered, and in so doing clears out the catalyst from the connections. The inlet valves are then closed, and the temperature of the oil increased to 170° or 180° C. Any remaining traces of moisture or free fatty acids are distilled away by the high vacuum which prevails. On the oil attaining the correct temperature for reaction, the vacuum valve is closed and the high pressure hydrogen admitted by the lower connection. This hydrogen raises the pressure inside the autoclave to about 75 lbs., and the reaction commences.

The speed of the reaction may be ascertained by closing the hydrogen inlet valve. The rate at which the pressure falls inside the autoclave indicates the rate at which the operation is proceeding.

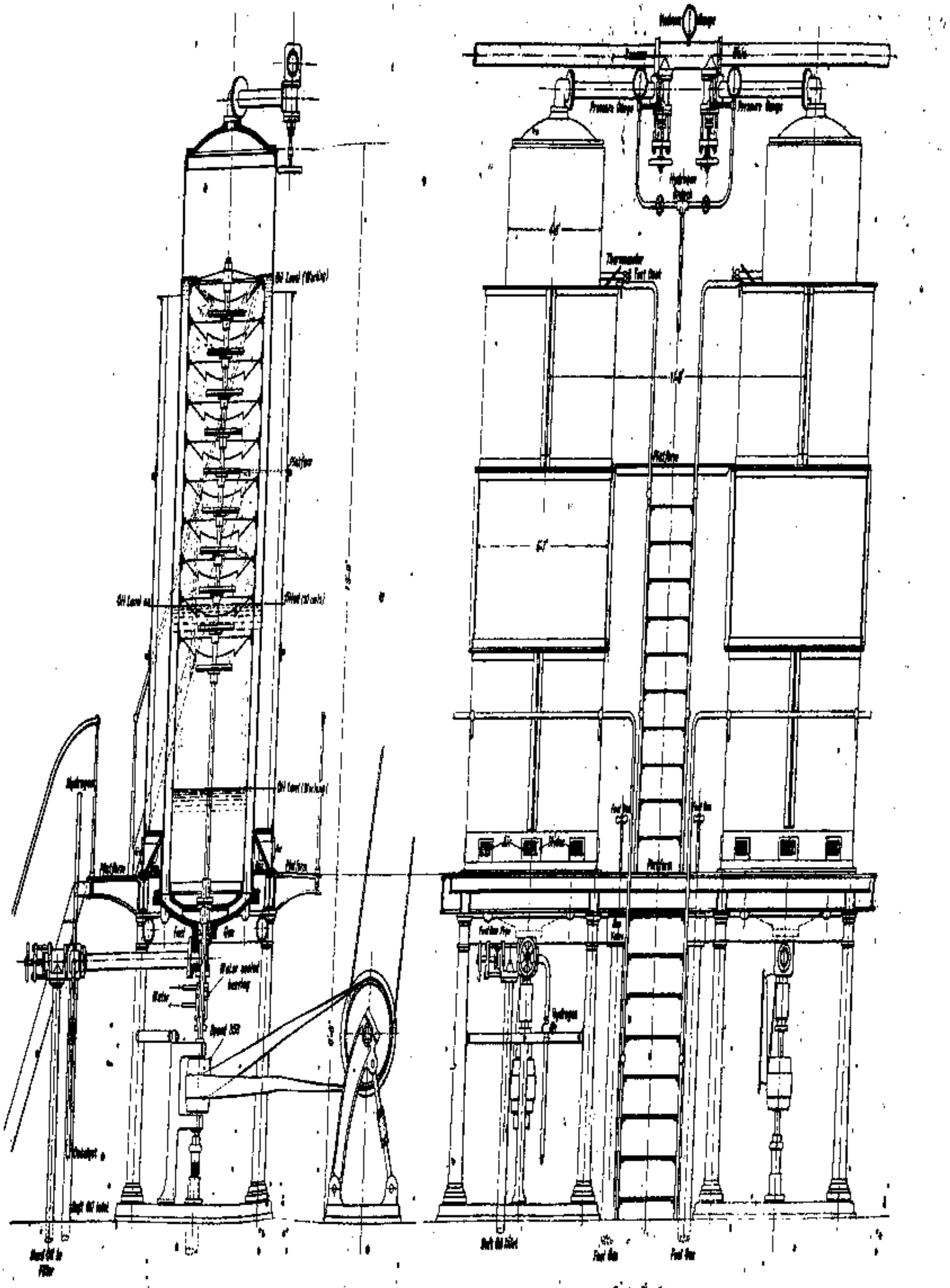


FIG. 64A.—LANE'S HYDROGENATING AUTOCLAVE. MODERN FORM.

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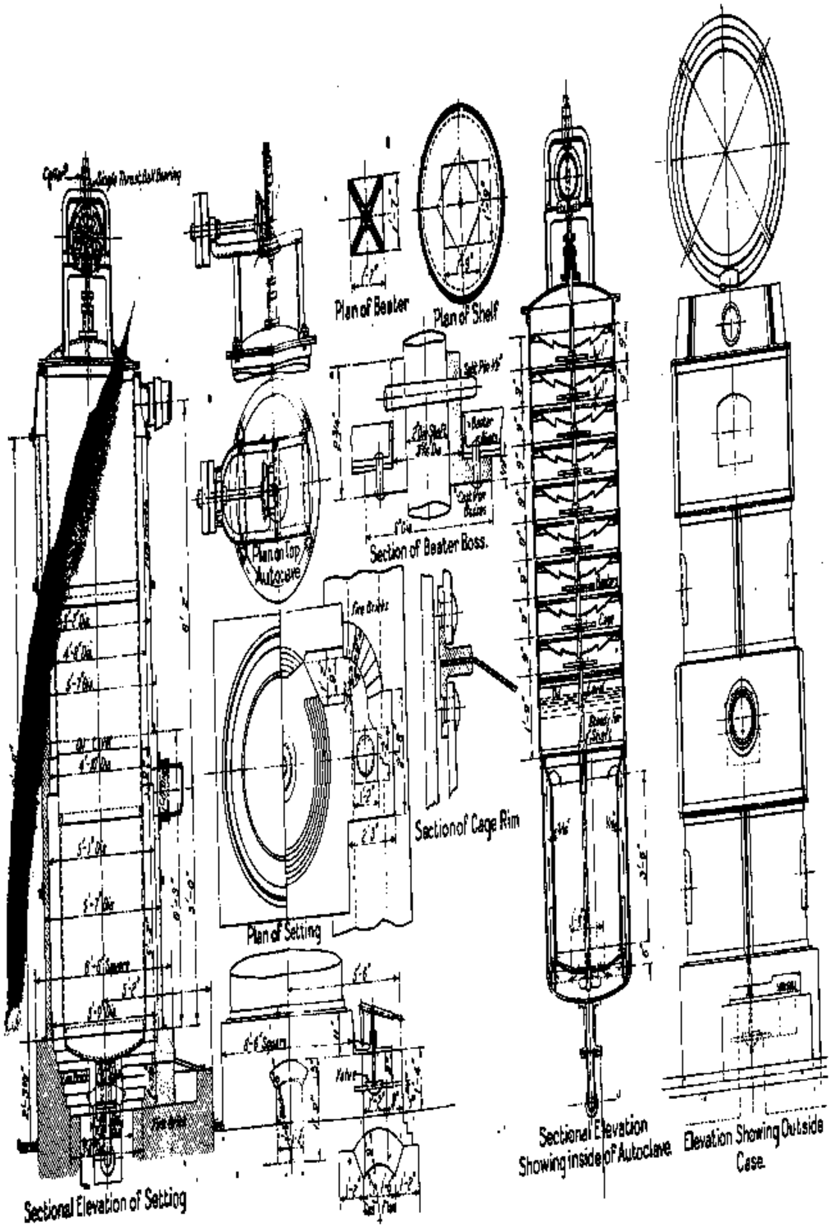

Plan of Beater

Plan of Shelf

Plan on Top Autoclave

Section of Beater Boss.

Plan of Setting

Section of Cage Rim

Sectional Elevation of Setting

Sectional Elevation Showing inside of Autoclave

Elevation Showing Outside Case.

Two to **three** hours is the usual time allowed for hardening. To ascertain when the operation is completed, samples are withdrawn by the test cock from time to time, and the melting or setting point observed.

As soon as the oil is reduced to the proper consistency the fuel gas heating the autoclave is turned as low as possible, without completely extinguishing the flames, the rotation of the atomiser shaft is stopped, and the oil is discharged from the autoclave into the **discharge cooler** by opening the outlet valve and permitting the hydrogen under pressure in the autoclave to act as an expulsive force. The autoclave is then immediately filled with a fresh charge.

The hardened oil flowing away from the autoclave is made to pass through pipes placed in a trench filled with hot water in order to prevent the oil setting and choking up the pipes.

In the **cooler discharge vessel** the hot oil is cooled out of contact with air in an atmosphere of hydrogen.

This is necessary for two reasons. Firstly, contact with air oxidises the hot oil and gives it an unpleasant taste and bad colour. Secondly, the oil as it comes from the autoclave is so hot that it will damage and possibly char the filter cloths if discharged directly through them without a previous cooling.

Each of the six hydrogenising autoclaves has its own cooler discharge vessel. The latter consists of a cylinder, 4 ft. in diameter and 6 ft. high, designed to take the charge from the autoclave, namely 1½ tons of oil.

Each vessel is fitted internally with a cooling coil of cold water, with inlet and outlet valves, with connections to the high and low pressure hydrogen supply, also with a pressure gauge, test cock, and thermometer and mercury pocket, so that the temperature of the oil passing into the filters may be observed and regulated by the cold water coil.

The oil, when sufficiently cooled, is now pumped out from the cooler discharge vessel through the filter presses, in order to free the oil from catalysts.

These **filter presses,** one to each autoclave, consist each of twenty-four plates, each 24 in. square. The filter presses are also provided with hot water heating, so that the oil will not solidify in them and block them up. The first runnings of oil are always contaminated with catalyst, and are run into a separate tank for returning to the filter, but afterwards the oil runs clear through the filter presses. The first runnings are then pumped through the filter once more, and so freed from catalyst.

Each of the oil tanks fitted to the filter is provided with heating coils to maintain the oil liquid.

The cake of catalyst left in the filter presses is removed and used over again with fresh catalyst. With care, this can be done four or five times.

The oil thus obtained is pumped from the oil storage tanks into casks. If it is necessary to store at the works the oil may be pumped into large storage tanks, with a capacity of 20 tons of oil, each tank being fitted with heating pipes to keep the oil liquid. The pumps deliver 100 gallons of oil per minute.

The **catalytic material** used in the Lane process is nickel deposited upon kieselguhr, and reduced *in situ*.

The success of the operation depends upon preparing the catalyst correctly.

The catalyst is prepared as follows:—

Take 4 cwt. of nickel sulphate and dissolve in 8 cwt. of hot water in one tank with a capacity of 20 cwt.

Take 4 cwt. of sodium carbonate and dissolve in 8 cwt. of water in another tank of the same capacity.

Take 3 cwt. of kieselguhr (clean best quality free from sand) and emulsify it in 6 cwt. of hot water in a tank of capacity 40 cwt.

To the tank containing the kieselguhr emulsion add the contents of the nickel sulphate tank, thoroughly stirring the materials together until thoroughly mixed. Now add very slowly the sodium carbonate solution, and boil the mixture for one hour to ensure the granulation of the precipitated nickel carbonate.

The particles of kieselguhr have now become coated with an adherent film of nickel carbonate, while the sodium carbonate has been transformed into sodium sulphate.

The solution is now passed through a filter press which will just hold the solid precipitate.

The sodium sulphate solution is run to waste. (If some unprecipitated nickel is still contained therein more sodium carbonate is added, and the precipitated nickel carbonate collected.)

The cake thus obtained of kieselguhr impregnated with nickel carbonate must be thoroughly washed free from all traces of sulphate. This is sometimes done in the filter press itself by means of hot water. The easiest way, however, is to remove the cake from the filter press, break it up, re-emulsify it with water, and again filter, repeating the process five times at least.

The carefully washed cake is removed from the filter press, dried in a hot air chamber, ground, and sifted. It is then carefully heated upon a tray or sheet of iron until all decrepitation ceases. The powder is next reduced to nickel in an atmosphere of hydrogen. This operation is conducted in a special machine invented by Mr Lane.

It consists of a closed vessel, heated by gas, and provided with stirring arms. The air inside is replaced by gas, then the heating is started. The machine is fitted with a condenser, and the water formed by the reduction passes over. The reduction is known to be complete when water ceases to come over.

The temperature of the reduction lies between 250° and 300° C.

When the reduction is completed, the arms are reversed so as to throw the reduced material into a bath of oil, without allowing it to come into contact with air.

The catalyst material is thinned out with oil to enable it to be added to the autoclave.

Each ton of oil to be hardened requires about 15 lbs. of metallic nickel, *i.e.*, 84 lbs. of the dried cake, before reduction.

The hydrogen used in the process, as explained before, must be as pure as possible. To produce 2 tons of hardened oil per hour a minimum supply of 7,000 cub. ft. of hydrogen gas per hour is needed.

The hydrogen is produced by the well-known **Lane** process, which is described in the author's book, "Industrial Gases," to which the reader is referred for further particulars.

The process is briefly this :—

Steam is first passed over hot iron in a suitable furnace, when hydrogen and iron oxide are produced, thus :—

$$\underset{\text{Iron.}}{3Fe} + \underset{\text{Steam.}}{4H_2O} = \underset{\text{Iron oxide.}}{Fe_3O_4} + \underset{\text{Hydrogen.}}{4H_2}$$

When the iron is oxidised it is again reduced by passing water gas over the mass :—

$$\underset{\text{Iron oxide.}}{Fe_3O_4} + \underbrace{2H_2 + 2CO}_{\text{Water gas.}} = \underset{\text{Iron.}}{3Fe} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Carbon dioxide.}}{2CO_2}$$

The water gas itself is produced by blowing steam through red-hot coke :—

$$\underset{\text{Steam.}}{H_2O} + \underset{\text{Coke.}}{C} = \underbrace{CO + H_2}_{\text{Water gas.}}$$

In the Lane system the iron is derived from spathic iron ore ferrous carbonate, $FeCO_3$. This is calcined, when it becomes ferrous oxide, FeO, and in this form is placed in the retorts.

The water gas used to reduce the iron oxide to metallic iron must be carefully purified to remove sulphur dioxide, sulphuretted hydrogen, water, etc. When the reduction is complete the supply of purified water gas is cut off, and steam at a low pressure is admitted to the retorts. The first portions of hydrogen which come off are contaminated with part of the reducing gas, water vapour, and carbon dioxide lingering in the retorts as the result of the previous reduction process. It is, therefore, not sent into the hydrogen holder, but burnt under the retorts.

After the plant has been working for some time the iron gradually loses its activity, and in the end almost ceases to react with the steam to produce hydrogen.

This is due to the fact that sulphur compounds and other impurities attack the iron, and form bodies which are not easily reduced by steam. This state of affairs is remedied by periodically passing air through the mass of iron backwards, so as to oxidise away the sulphur and other impurities.

From this brief description it will be seen that the **Lane hydrogen plant** consists of (1) the **hydrogen retort** furnace containing the iron oxide, which is periodically oxidised by steam from (2) a **steam boiler**, and reduced by gas from a (3) **water gas producer**, attached to which are (4) **purifiers** for the water gas, and (5) a **gasholder** for the water gas; (6) a **gasholder** for the hydrogen (this is the low pressure hydrogen supply referred to in the text above); (7) compressors for the hydrogen gas; (8) reservoirs for high pressure hydrogen for sending into the autoclaves.

By referring to Fig. 61, p. 107, the plan of the Lane's hydrogenising works, the relative position of these various pieces of apparatus may be seen.

The **hydrogen compressors** pump the hydrogen direct from the low pressure gasholder of the hydrogen generating plant of the establishment into the high pressure hydrogen reservoirs.

The **hydrogen compressors** should be in duplicate (in case of failure), and should be capable of compressing 10,000 cub. ft. of hydrogen gas per hour at atmospheric pressure to a pressure of 250 lbs. per square inch.

The **storage reservoirs** into which the hydrogen is compressed at 250 lbs. are tested hydraulically to 500 lbs. per square inch. At this pressure all pipes and valves should be perfectly sound, as large amounts of hydrogen may be lost through apparently small leakages, since hydrogen is a very thin, light gas, and rapidly diffuses. The capacity of the **compressed hydrogen reservoirs** is 714 cub. ft. This corresponds to a storing capacity of 10,000 cub. ft. of free hydrogen measured at atmospheric pressure and then compressed to 250 lbs. per square inch, allowing for increase of temperature after compression.

The reservoirs may be built up of large tubes or of multiple vessels. They must be provided with a perfect drainage, so that any water condensing in the low lying parts of the reservoir may be blown away by means of readily accessible test cocks.

As stated above the oil is only treated with hydrogen at a pressure of 75 lbs. per square inch, and consequently the pressure of the gas from the reservoirs is let down by an automatic regulator to this value.

One reason for compressing the hydrogen so strongly into the reservoirs is to dry it. Strongly compressed hydrogen deposits much of its moisture on cooling, and the use of the driest possible hydrogen is important.

No atmospheric air or oxygen must be allowed to leak into the hydrogen, as this will discolour the oil and damage the catalyst.

The whole works will require about 50 H.P. to drive it with a sufficient reserve to provide for contingencies.

Steam is required for operating the fuel gas plant. The entire **heating of the plant** is effected by the medium of cheap fuel gas.

Mr Lane does not favour the employment for this purpose of superheated steam, because the use of such entails costly high pressure construction and very high pressure steam boilers. Moreover, there is a considerable risk of leakage into or out of the vessels owing to the disruptive effects of unequal expansion or contraction. In the event of water obtaining access to the highly heated oil explosion may result.

The **fuel gas** is generated in a continuous manner from coke, coal, lignite, or other fuel. The gas is generated under slight pressure (say 2-3 in.), and is cleansed from mechanical impurities, and delivered into a gasholder which provides a uniform and steady supply of heating gas to the various autoclaves and heating pans. The gas is **producer gas** of calorific value 150 thermal units per cubic foot. **Water gas** is too costly for use for heating purposes.

Geoffrey Martin's Process.—A new principle for mixing and heating the oils was introduced by Geoffrey Martin in an English Patent, No. 129,461 (16th July 1918). In this apparatus all mixing gear, baffle plates, etc., are avoided in a very simple manner. The apparatus is shown in Fig. 62c, p. 112.

The charge of oil (which may have been preheated to a suitable temperature) is placed in a reservoir 5, whence it flows down a series of tubes 6, 6, 6, which may be horizontally placed or vertically placed. These tubes are heated by a steam jacket (as is shown in the attached diagram). The oil flowing down the pipe 6 is sucked in by the pump 4 and thrown up the pipe 3 back again into the reservoir 5, so that the oil is maintained in continual circulation through the reservoir and pipes.

The heating of the oil is thus effected not in the reservoir 5 but by means of the steam jackets surrounding the pipes 6. As the pipes can be made of any length the heating of the oil can be made to take place very rapidly, and the temperature of the heated oil is regulated by a thermometer or thermoindicator in the pipe as shown.

The mixing of the hydrogen with the oil is also effected in the pipes 6, 6, 6 as follows:—Projecting into the pipe 6, 6, 6 is a series of perforated pipes 7, 7, 7, closed, or partially closed, at each end. The hydrogen gas is forced by the pump 8 into these pipes through the pipe 9 until the requisite pressure of hydrogen is attained. The circulation of hydrogen in the apparatus is maintained by the pump 10 which draws the gas from the top of the vessel 5 and forces it down the tube 9 and then into the tube 7, where the gas rushes out through the perforations into the descending oil, so that there is a continual circulation of oil going on in the one direction and a stream of hydrogen passing up through the oil in the other. As the pipes are narrow the hydrogen and oil are very intimately mixed in the pipes, thus rendering unnecessary the use of baffle plates, stirring gear, and similar plant for the purpose.

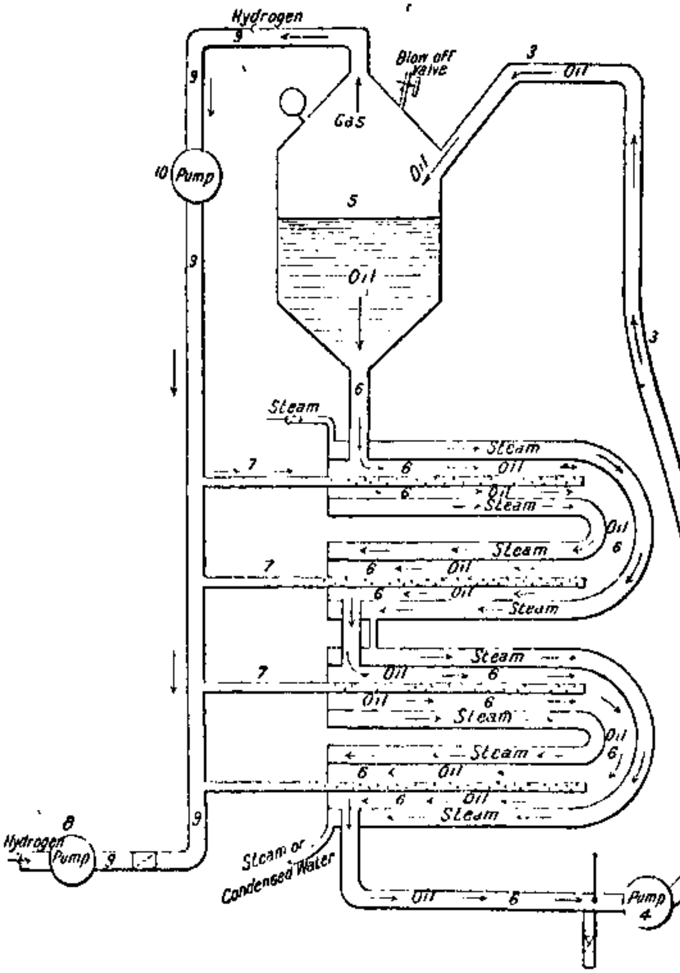

FIG. 62C.—Geoffrey Martin's Oil Hydrogenation Process.

In a second patent applied for on 27th November 1918 (19,567, 1918), Geoffrey Martin makes his process continuous. The apparatus is shown in Fig. 63. The oil to be hardened is pumped in a steady stream into a pre-heater 1, and then flows out in a carefully regulated stream through the tube 2. At the point A it meets the oil from the tank M, which oil is forced in through a force pump B. The oil in M is impregnated with catalyst, and consequently, the oil-containing catalyst mixes with the larger volume of oil devoid of catalyst coming from the pre-heater 1, and the rate of flow of oil from M and from the pre-heater I is so regulated that proper amounts of catalyst are introduced into the oil so as to cause hydrogenation to take place properly. The oil now mixed with catalyst is pumped by means of C up the tube 3 into a reservoir 5, and continuously flows down a series of tubes 6, 6, 6, which may be of very considerable length, and which are heated externally by steam, hot air, or other heating medium. Inserted into each of the tubes 6, 6, 6 is a series of perforated pipes 7, 7, 7, through which the hydrogen is forced, and which churns up and mixes with the oil as it flows down the tubes as described in the previous patent. The oil, by the time it has passed through all the tubes and has reached the outlet D, is hardened sufficiently, and passes away through the cooler E, and then is forced through a pump F to a filter press G or other arrangement for removing the catalyst. From G it passes to the storage tanks. The rate at which the oil is hardened depends upon the length of the pipes 6, 6, 6, through which it passes, and the quantity of hydrogen gas it meets in passing down the pipes. Also the purity of the hydrogen and the sensitiveness of the catalyst are important factors. Consequently, by making the passage through the pipes 6, 6, 6 sufficiently long, and causing it to meet a sufficient quantity of hydrogen during its passage, the oil emerging at E, can be hardened to any required degree.

The advantages of a continuous counter-current process are obvious. In ordinary processes large masses of oil, weighing a ton or more, are treated in batches in massive autoclaves, whereas in the present process the oil is fed in a thin stream through long tubes, without at any moment of time a great mass of oil being under treatment. Thus danger of explosion or fire are largely obviated. A large quantity of hydrogen can also be forced against a small amount of oil, so that the latter is rapidly hydrogenated without prolonged heating, thereby avoiding deterioration in quality.

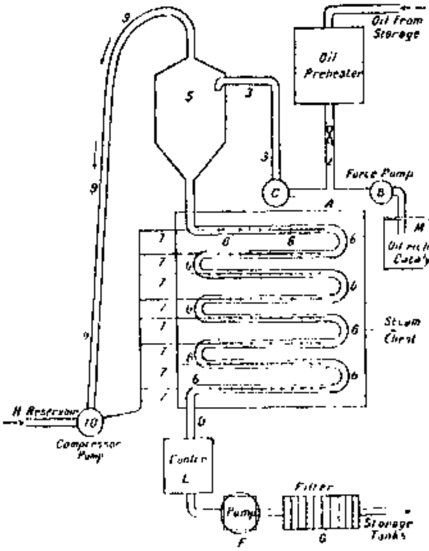

FIG. 63.—Geoffrey Martin's Continuous Oil Hydrogenation Process.

The Kayser Process (United States Patent, 1,004,035, 1911) consists in mechanically agitating the oil and catalyst in presence of hydrogen under pressure. The apparatus described in the patent is shown in Fig. 64.

A horizontal jacketed drum is closed by stuffing boxes at each end, and contains working paddles covered by gauze. A pump A draws hydrogen from a three-way valve B and passes it through C into the vessel. The vessel is one-fourth to one-fifth full of oil and catalyst. Unabsorbed hydrogen is blown off at D. The oil is run out at E. The temperature of hydrogenation is 150° C. to 160° C. Kieselguhr is suggested as a carrier for the catalytic nickel. (United States Patent, 1,008,474, 1911.)

Wilbuschewitsch Process (see United States Patent, 1,079,278, 1913; also U.S. Patent, 1,024,758, of 1912; English Patents, 15,440, 1911; 72, 1912). The apparatus is shown in Fig. 65, p. 115.

The vessel R contains the fat to be treated, and the vessel O contains the catalyst. Pumps A, A_1 feed the oil and catalyst into a mixing device B, by which an intimate spray of catalyst and oil is obtained. The mixture passes through a pipe G and a valve H into an autoclave J$_1$, which is furnished with a spraying device C$_1$ which consists of a number of nozzles so arranged that the oil and catalyst are uniformly sprayed into the whole inner space of the autoclave. A compressor K forces hydrogen into the autoclave under a pressure of nine atmospheres, the hydrogen passes through a pipe X, which extends from the upper part of the autoclave downward to its lower end, and terminates in an admission nozzle D$_1$. By this spraying system an intimate contact of oil and hydrogen on the counter-current principle takes place. The autoclave is heated to 100°-160° C. The partially hydrogenated oil collects in the conical part of the autoclave, and is sprayed in the form of a fountain through the autoclave by the incoming hydrogen. The oil from the first autoclave J$_1$ is forced by a pump E$_1$ into the second autoclave J$_2$, the hydrogen entering through the pipe J$_2$, and the actions occurring in the first autoclave are repeated.

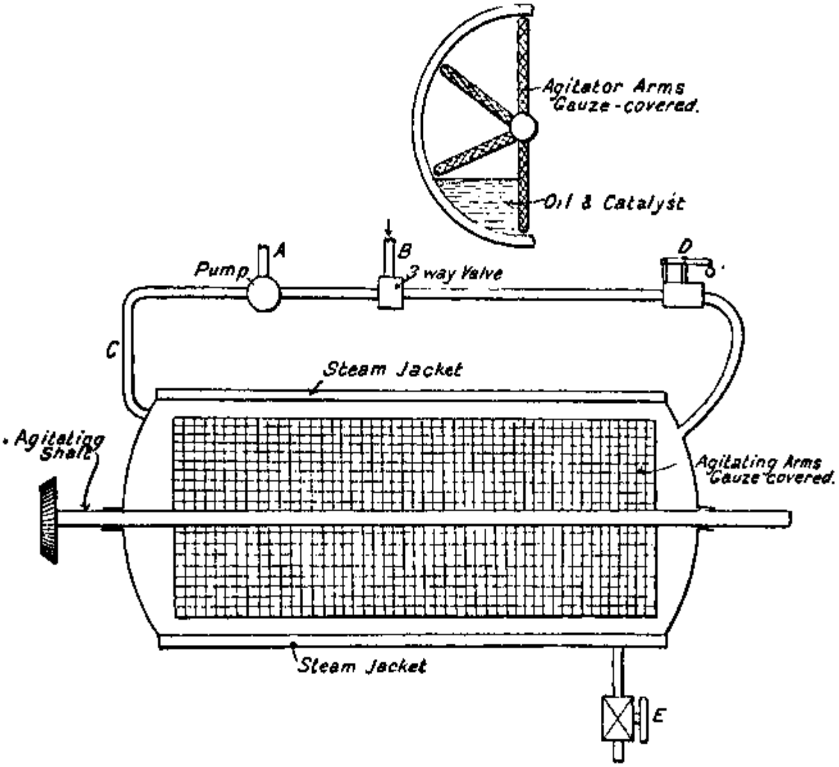

FIG. 64.—Kayser Process for Hydrogenating Oil.

Several autoclaves can be arranged in series in this way. When the fat is sufficiently hardened (determined by withdrawing a sample and determining the melting point or iodine value) the oil and catalyst mixture is run out through the valve U into the centrifugal apparatus F, where the oil is separated from the catalyst. The clear oilruns into the tank N$_1$, while the catalyst passes through the pipe R^1 and the valves S and T to the vessels O and P. Spent catalyst is run into the tank P to be regenerated. Fresh catalyst is introduced through the valve T. Unabsorbed hydrogen passes through the check valve W and the pipe Q and cooling worm L into a washing vessel M filled with caustic soda lye, where it is purified and passed on to the compressor and autoclaves.

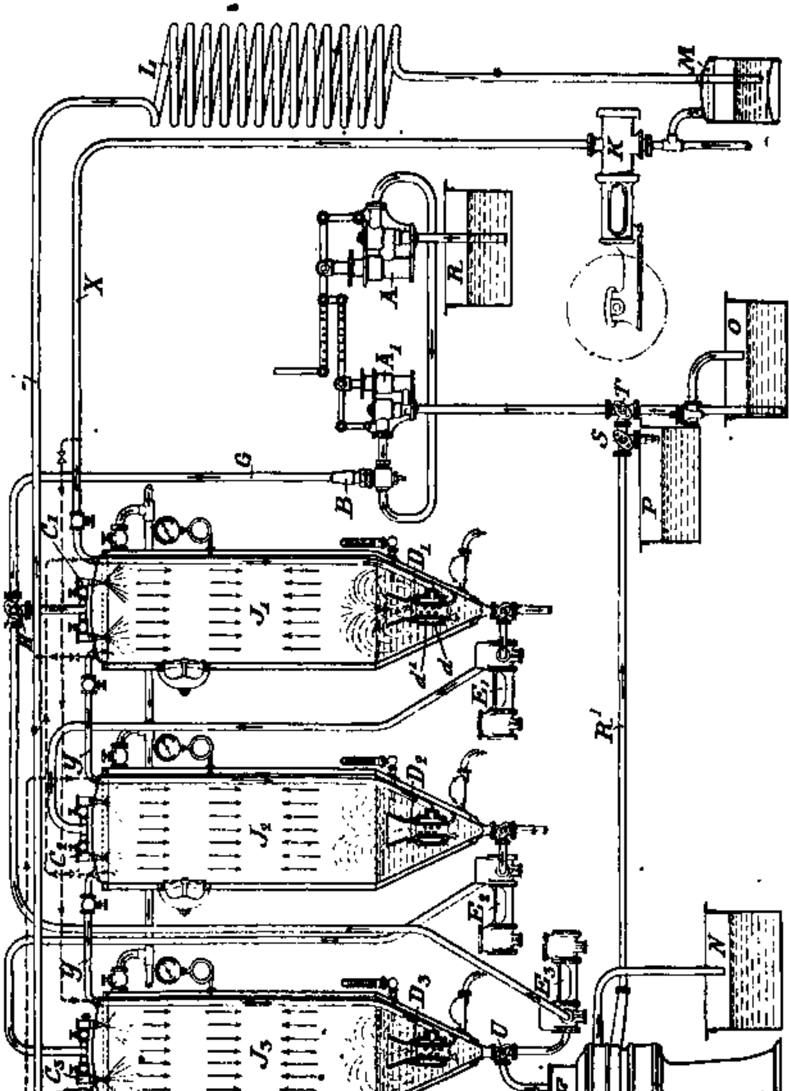

FIG. 65.—Wilbuschewitsch Process for Hydrogenation of Oils.

Testrup's Apparatus (English Patent, 7,726, 1910) is also based on a spraying system. The apparatus is shown in Fig. 66. It consists of a series of closed autoclaves *g*, *o*, *s*, *t*, in which oil and catalyst are sprayed in series into hydrogen gas at a continually decreasing pressure.

Thus in *g* the oil, heated to 160°-170° C., is subjected to hydrogen at 15 atmospheres pressure. In *o* the hydrogen is at 12 atmospheres pressure. This difference in pressure causes the oil to spray from *g* into *o*. *s* has a hydrogen pressure of 9 atmospheres, and, consequently, oil sprays from *o* into *s*. The oil and catalyst are thus sprayed several times into gas at successive lower pressures. The oil enters by the pipe *f* and the hydrogen by *k*; *n* is a reducing valve for regulating the pressure of the gas in the next autoclave; *h* shows heating tubes for superheated steam; *l* is the pipe carrying the oil to the spray nozzle *p*. The oil is pre-heated to 160° C. in the vessel *a* which is provided with stirring arms. r is the storage tank for the oil, while *w* is the filter press for removing catalyst from the treated oil; *y* is the treated oil tank.

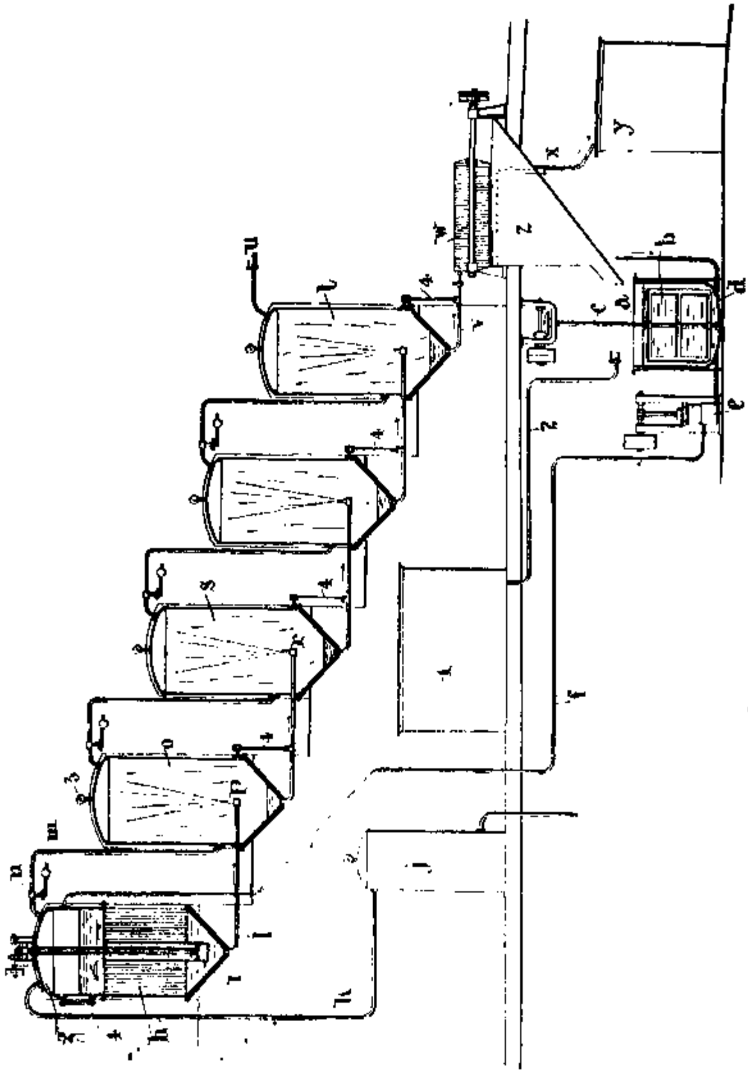

FIG. 66.—Testrup's Process for Hydrogenation of Oil.

It should be noted that both Wilbuschewitsch and Testrup's system refer to the "spraying" or "atomisation" of the oil into the hydrogen. A number of patents exist, the object of which is to bring the catalysts, oil, and hydrogen into intimate contact. Yet all that is apparently needed is a gentle mixing of the contents, as very rapid diffusion takes place.

Ellis (U.S. Patents, 1,026,156, 1912; 1,052,469, 1913; 1,040,531, 1912; also British Patents, 24,084, 1912; 16,782, 1913; 16,600, 1914) uses tubes filled with catalysing material in granular form, and allows the oil to flow through the tubes in one direction while passing the hydrogen in an opposite direction.

Fig. 67 shows a vertical type of apparatus, the catalyser being shown at C in the tube A. Oil enters by the pipe O and passes into the tube or cylinder A. The pump P causes the oil to circulate from the top to the bottom of the apparatus through the pipe B. Hydrogen gas admitted at H is pumped to the bottom of the cylinder A, and the excess is withdrawn at the top by the pipe D, passing through the drier E and back into the treating cylinder. In another form of apparatus Ellis arranges the catalyser in beds or trays, instead of in a bed of considerable depth. See United States Patent, 1,040,531, 1912.

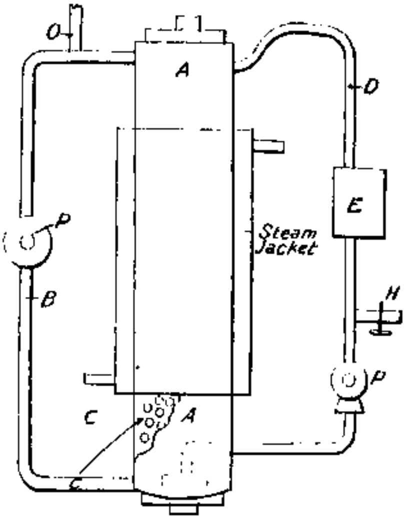

FIG. 67.—Ellis's Process for Hydrogenation of Oil.

Calvert (English Patent, 18,350, 1913) mixes the oil and gas by means of a rotary stirrer driven by an electric motor contained in the autoclave itself, and under a hydrogen pressure equal to that at which the reaction is carried out.

(2) **Wet Processes.**—In these processes the catalyser is generated in, and not without, the oil to be hardened. A compound of nickel is introduced into the oil (or part of the oil) to be hardened, and the whole is heated while a stream of hydrogen is passed through. The nickel is thus produced *in situ*.

Three processes have been worked on a large scale:—

1. **The Bedford-Erdmann Process** (see English Patents, 2,520, 1907; 29,612, 1910; 27,718, 1912; 28,981, 1912; United States Patent, 949,954, 1910; German Patents, 211,669, 1907; 221,890, 1909).—Nickel oxide is introduced into the oil, which is heated to 255°-260° C. Hydrogen gas is then passed through, which reduces the oxide to the metallic state with the liberation of water (see United States Patent, 1,026,339, 1912).

The disadvantage of the use of nickel oxide is the high temperature that it is necessary to employ in order to cause reduction, this temperature being close to the temperature of decomposition of the fat. A partially decomposed fat causes a bad colour and taste in the hydrogenated oil.

Erdmann introduced certain improvements into this process, producing the oxide by special processes. The oxide, for example, is produced from the nitrate instead of from the sulphate (see *Siefen. Ztg.*, 1913, 1413; also German Patent, 211,669, 1907).

A small factory was erected at Sleaford, England. A company, called the "Ardol Co., of Selby," is stated to be working the process. In Germany the "Ammendorfer Oelhartungswerke" is stated to have adopted the process.

A great advantage of the process is the fact that a very impure hydrogen can be used in this process. It has been stated that the Ardol Company of Selby use the Caro-Linde process for hydrogen, liquefying water gas, and separating the uncondensed hydrogen from the liquid carbon monoxide.

A difficulty in this process is the filtering of the oil free from catalyst. The nickel suboxide appears to be in a colloidal condition and soon blocks up the filter cloths.

Sedimentation is said to be resorted to in addition to filtering, the oil being run into tanks and allowed to stand until the bulk of the nickel catalyst has settled out. It is only after the bulk of the nickel has thus been removed that the oil is sent through the filter cloths.

Attempts to destroy the colloidal condition of the nickel salts by the use of electrolytes such as salt or alkali, are stated to have led to improvements in the process.

2. **Wimmer-Higgins Process** (see English Patents, 25,326, 18,282, 1912; 23,377, 1912; 4,144, 1913; 4,665, 1914; also United States Patent, 1,081,182, 1913).—Here the nickel is introduced into the oil in the form of salts of organic acids like formic, oxalic, or lactic acids.

These salts are much more easily reducible than oxide of nickel, so that overheating is avoided.

It has been objected, however, that on heating carbon monoxide is split off (which acts as a catalytic poison), and that the organic acids are liberated, which attack the apparatus. In Germany a company to work the process has been formed called the "Fettraffinerie A.G., Bremen und Brake."

3. **Process of the Norsk Hyderings Company** (see English Patent, 11,540, 1913; 11,543, 1913).—In this process nickel carbonate is the salt of nickel employed, which is reduced in oil at a lower temperature than the oxide, and is stated to be free from the defects of the Wimmer-Higgins process The company hold Fuch's patents.

The process of reduction is thus described in Fuch's patent, No. 11,542, 1913:—

"1,000 (one thousand) kilograms of castor oil are mixed with 1.2 per cent. of finely-powdered and freshly-prepared nickel carbonate previously dried at 110° C., and the mixture is then heated to 230° C., whilst a current of hydrogen is slowly allowed to pass through the same; as soon as this temperature of 230° C. is attained, highly-compressed hydrogen (say from 12 to 15 atmospheres) is admitted into the mixture through a capillary nozzle. The reduction of the salt to metallic nickel takes place under the well-known characteristic phenomena, namely, with slight frothing due to the formation of water. As soon as this operation is completed, the temperature is lowered, and the reduction of the oil carried out as an uninterrupted continuation of the preceding operation."

In a second patent of Fuch's, No. 11,543, 1913, held by the company, the following conditions are laid down for increasing the speed of the hydrogenation:—

"An essential increase of the speed of the reaction is obtained by maintaining the oils under treatment at a moderate temperature of from 90°-150° C., while the reducing gas is heated to a higher temperature, namely, say from 200°-250° C.

"The avoidance of a too high heating of the mass itself has a favourable influence upon the final product, whereas the heating of the reducing agent appears to produce an increase of its activity. Comparative experiments have shown that by these means the speed of the reaction can be increased to the extent of over 10 per cent.

"Care must be taken to increase the efficiency of the reducing gas by a preceding splitting of its molecules into atoms. This can be done by subjecting the gas to chemically active rays. A dissociation of the hydrogen also appears to take place when it is conveyed over catalytically acting substances, such, for example, as spongy platinum or freshly-prepared metallic nickel. The dissociated hydrogen possesses, as has been proved by comparative experiments, an increase of activity of from 15-20 per cent. The catalytic substance can be located within a suitably long pipe or upon trays of a column apparatus, and the necessary heating may be effected by way of example by means of a heated oil casing."

This process is worked on a very large scale by the following companies:—

Norway.—The Vera Fedtraffineri A.S., Sandefjord. Capacity, 16,000 tons per year. Edible and industrial fats.

Sweden.—Aktiebolaget Henriksborgs Fabriker, Stockholm. Capacity, 10,000 tons per year. For hardening vegetable oils for industrial and edible hard fats.

Denmark.—A.S. Oliehaerdningsfabriken, Kjobenhavn. Capacity, 8,000 tons. Edible fats from soja bean oil.

Holland.—Jan Dekker, Wormerver. Capacity, 4,000 tons.

Belgium.—De Bruyn, Ltd., Termonde. 10,000 tons. Edible fats.

France.—Societe de Stearinnerie et Savonnerie de Lyon. 8,000 tons. For candle and soap manufacture.

Italy.—"Corisoleum" Societa Italiana per l'Industria degli Olii, Mira. 16,000 tons. For candles, soaps, and edible fats.

Germany.—Centra A.G., Krischwitz, Elbe. 20,000 tons for candles, soaps, and edible fats.

Roumania.—Phenix Societate Anonima Romana, Bucharest. 4,000 tons for edible fats.

(3) **Gaseous Processes.**—In these the nickel is passed into the oil in the form of an unstable gaseous compound, namely, nickel carbonyl.

This is decomposed in the oil, depositing the nickel, and liberating the carbon monoxide.

Shukoff (see German Patent, 241,823, Jan. 18, 1910. *Also* H. Kamps, Belgian Patent, 246,975; United States Patents, 738,303, 777,848, 943,627) seems to have been the first to have claimed the process of hydrogenating oils by means of nickel derived from the decomposition of nickel carbonyl.

The carbonyl is obtained from reduced nickel by passing carbon monoxide over it at a low temperature. The carbonyl is soluble in oil, and when the solution is heated to 200° C., the nickel is set free and can be used as a catalyser.

It is stated by some authorities, however, that the carbon monoxide acts as a catalytic poison for the nickel.

Lessing (British Patent, 18,998, 1912) has worked out a process for the hydrogenation of oils by the use of nickel carbonyl, which is being worked by the Hydronyl Syndicate, Ltd., 140 Leadenhall Street, London.

The system is worked on the counter-current principle. A gas composed of hydrogen and a small amount of carbon monoxide is passed over nickel contained in a container and heated to a suitable temperature. The carbon monoxide takes up the nickel, and the gas then passes into the oil heated to 160°-200° C. The nickel carbonyl decomposes in the oil, setting free the nickel in a nascent condition. The hydrogen present then acts in the presence of this catalytic nickel, and hydrogenises the oil. The presence of carbon monoxide is stated not to poison the nickel to such an extent as to stop the rapid action of the nickel, because the nickel is liberated in an atomic condition, and acts so rapidly in this condition in the presence of excess of hydrogen that the poisoning or slowing effect of the carbon monoxide on the nickel does not have practical results.

In Lessing's process only ordinary atmospheric pressures need be used, and a temperature of about 180° C. is required to decompose the nickel carbonyl passing through the oil. A maximum amount of 0.1 per cent. metallic nickel is used. The nickel may be recovered from the oil either by filter-pressing or centrifuging in suitable apparatus.

In the ordinary processes of oil hardening the nickel catalyst must be recovered by dissolving in sulphuric acid (or other acid), making into nickel sulphate (or other suitable salt), then precipitating as carbonate and reducing again. In the Lessing process, however, this procedure is avoided by returning the scrap nickel catalyst into the volatiliser, and passing carbon monoxide over it. The carbon monoxide picks up the nickel, and the nickel-containing gases pass once more into the heated oil. The process can be worked continuously, oil travelling in one direction and the gases in the other. The carbon monoxide can be recovered and used over and over again.

Costs of Hardening Oils

Estimates relating to the cost of hardening oils are, for many obvious reasons, difficult to obtain.

The following figures, supplied by Mr Lane, relate to his process, and the prices quoted therein apply to pre-war days. The figures, however, are very instructive, and are founded on data taken from a Lane plant producing 1 ton of hardened oil per day:—

Cost of Hardening 1 Ton of Linseed Oil.

	£	s.	d.
Hydrogen—3,530 cub. ft. at 4s. 6½d. per 1,000 cub. ft.	0	16	0
Loss of Catalyst	0	14	0
Fuel for Heating—1 cwt. coke at 30s. per ton	0	1	6
Power	0	1	0
Steam—1,344 lbs. at 3s. 4d. per ton	0	2	0
Water—400 cub. ft. at 10d. per 1,000 cub. ft.	0	0	4
Filter Cloths—1 yard at 1s. 3d. per yard	0	1	3
Labour (including preparation of catalyst)—7 men at 6d. per hour	0	3	6
Running Repairs	0	2	0
Total	2	1	9

Nickel sulphate at 42s. per cwt., **kieselguhr** at 17s. per cwt., **carbonate of soda** at 55s. per ton.

Referring to these figures, it will be seen that the heaviest item appears to be hydrogen; and indeed the whole problem of hardening cheaply appears to be essentially the problem of producing pure hydrogen cheaply. The recent great improvements in hydrogen manufacture will, no doubt, bring this figure down.

The item "loss of catalyst" is serious. The cost of labour is, at the present time, much too low. Also nothing is placed against depreciation of plant. It will be noticed, too, that the cost depends largely upon the nature of the oil treated. Thus a heavy unsaturated oil like linseed requires a much greater quantity of hydrogen and a much longer time than a more saturated oil, such as cotton-seed. On the other hand, a fish oil like whale oil may require more hydrogen than linseed.

The author has heard it stated that the nickel suboxide process cost, to harden per ton of linseed, about £6 to £7 in pre-war days, and at the present time about £14. These figures give some idea of the cost of hardening oils, although exact estimates have never been published.

On p. 123 we give the very instructive Costs of Hardening Fats obtained by the Centra A.G., Krischwitz, Elbe, which the reader should study.

Uses of Hardened Fats.—The process of hardening fats has now become of great industrial importance.

The world's supply of hard natural fats is insufficient to meet the wants of commerce. The supply of liquid oils, on the other hand, is abundant. The object of hardening oils is to convert the superabundant liquid oils into hard fats like tallow.

(*a*) **Use of Hardened Fats in Soap-Making.**—The best soap-producing fat is a hard fat like tallow. It yields a firm soap.

Unfortunately, so much of the natural supply of hard fats is now employed in the making of margarine and other foodstuffs, that the amount of such fats available for soap-boiling and candle-making has seriously diminished.

Owing to the increase in cost of tallow and the limited amount in which it is obtainable, the soap-maker within recent years has fallen back on other hard oils like palm and palm-kernel oil, coco-nut oil, etc.

These oils, also, are rapidly increasing in cost, and their use in other industries is increasing. The only other oils available in large amounts to the soap-maker are liquid oils like whale oil, soja-bean oil, and the like. Unfortunately, they yield soft, sticky soaps, so that by using these oils in the natural state the soap-maker obtains a product of inferior quality.

When, however, these oils are hardened, he obtains from them substances of a tallow-like nature (white, odorous, and hard), which make firm soaps without affecting the yield of glycerine from the oil—glycerine being a very valuable product of the soap-making industry.

The hydrogenation process thus gives to the soap-maker a wide range of oils which otherwise would be almost useless to him. Consequently hydrogenated and hardened fats are at present used largely for **soap-making** (see English Patent, 13,042, 1907). Although the soaps produced are hard and do not lather well, this difficulty could be got over by mixing the hardened fat with a suitable amount of another fat which would give the necessary qualities to the soap. Usually 25 per cent. of hardened oil is added to the natural oils.

The soap made from hardened fat is stated to give satisfactory results with a much larger percentage of resin than can be used in soap made from tallow or palm oil.

(*b*) **Use of Hardened Fats in Candle-Making.**—Candles require to be made of hard, firm, white material. Hydrogenated oils supply a cheap material for making candles, tallow and other high-class hard fats being very expensive to use.

(*c*) **Preparation of White, Hard, Inodorous Fats from Fish Oils.**—Fish oils in their natural state are usually discoloured, foul smelling, and low-grade liquids.

By subjecting them to hydrogenation, their unpleasant smell is completely removed, and they are turned into white, tasteless, odourless fats of tallow-like consistency. This makes the process particularly valuable. This deodorising effect, however, is only obtained if the hydrogenation is carried out nearly to completion.

Hardened **fish oils** must have their iodine value reduced to under 50 if they are to yield a suitable washing soap, devoid of all smell of fish oil.

Consequently, it is not possible to deodorise an oil by this process without hardening it, so that the process has little value for the makers of soft soap and other users of liquid oils.

It is stated that hardened whale oil may, after long standing, develop a fishy smell. In practice, however, the hardened oils are usually hardened at the soap works and turned immediately into soap, so that no trouble from this cause usually ensues.

Whale Oil is the chief oil subjected to hydrogenation, the world's supply in 1912 amounting to 1,200,000 barrels (42,000 tons). (See Offerdahl, *Ber. deutsch. Pharm. Ges.*, 1913, **23**,558, who states that there is a factory in Norway capable of producing 4,500 tons of H by an electrolytic method, and of hardening 150 tons of whale oil per twenty-four hours.)

Hardened whale oil melts at 40°-50° C., is devoid of taste and smell, and so is a valuable fat.

(*d*) **Use of Hardened Oils for Edible Purposes.**—Hardened **cotton-seed oil** and hardened **whale oil** are used for edible purposes, and no doubt the use of hardened fats in this respect will greatly increase in the future. They form excellent frying fats, and are now used in increasing quantities in the manufacture of margarine.

No difference between the digestibility of hardened fats as compared to that of natural fats has been found. Obviously, a hardened edible fat should melt below the temperature of the body in order to obviate indigestibility.

Hardened oils are stated to have been used in the manufacture of chocolate instead of the expensive cocoa-butter.

Many manufacturers of edible products betray great reluctance to use hardened oils. This is probably founded on the natural caution which those who deal with such essential commodities as foodstuffs must exhibit in order to safeguard their reputation. However, so far as is definitely known, no ill effects have been definitely traced to the use of hardened oils. Owing to the high temperature at which such oils are necessarily prepared it is quite certain that any traces of vitamines such as are always contained in natural fats must have been destroyed.

Consequently, a hardened fat should never be used alone, but should always contain a considerable portion of a natural fat. The objection that minute traces of nickel salts found in the hardened fats may act poisonously does not appear to have any weight in practice.

Hardened fats differ from natural fats in that they appear to be more easily saponified by alkalis.

Leimdorfer (*Seifensieder Ztg.*, 1913, **40**, 1317) suggests that hardened "stearin" is an allotropic modification of the natural glyceride.

(*e*) **Use of Hardened Fats for Transport.**—In the shipment of liquid oils heavy losses are occasioned by leakage and breakage.

The soja-bean oil producers of Japan and Manchuria are stated to be considering the advisability of hardening the oil before shipping abroad, since the hard oil, being solid, will not leak through the casks, etc.

(*f*) **Other Uses of Hardened Oils.**—Hardened fats are now used for lubrication purposes. In the tanning industry, stearin, produced by hydrogenation, has been employed instead of oleo-stearin.

Principal Oils Hardened

The principal oil hardened is **whale oil.** Most fish oils are now hardened in order to increase their value.

Increasing quantities of **linseed, cotton-seed, soja-bean,** and **coco-nut** and other oils are now hardened.

Coco-nut oil is hardened (although, naturally, a fairly hard substance), because its value and appearance is thus increased, and it loses the characteristic smell of coco-nuts.

It is stated, however, that hardened coco-nut oil, if kept for a long time, sometimes develops the characteristic smell of the parent oil.

Nickel in Hardened Fats.—An oil hardened by a process which includes Ni as a catalyst, may contain 0·5-2 mg. Ni per kilo, and possibly deleterious effects might arise from the unlimited consumption of such oil. Normann and Hügel (*Halbmonatsschrift für Margarinindustrie*, 1913, VI., No. 17) showed that this quantity of Ni is often contained in foodstuffs prepared in nickel vessels, which have had no injurious effects on persons who have consumed them. Feeding trials with commercially hardened oils containing from 0·07-6 mg. of nickel per kilo have been carried out without ill effects ensuing (see Lehmann, *Chem. Zeit.*, 1914, **38**, 798).

Prall has found that nickel is found in fats only in *traces*, and then only when the oils used contain considerable amounts of *free acid.*

Sesame oil with 2.58 per cent. acid gave a hardened oil with 0.006 per cent. nickel oxide (Ni_2O_3); a whale oil with 0.61 per cent. free acid contained 0.0045 nickel oxide in the hardened fat; with only 0.2 per cent. free acid in the original oil, no nickel could be detected in the hardened product. Bower states neutral oils do not take up nickel (*Z. Nahr. u. Genussm.*, 1912, 104).

Testing for Hardened Oils.—The only reliable test is the presence of nickel in the oils.

To detect nickel, 5-10 gm. of fat (still better 2¼ lbs. [1 kilo] in cases where the amount of nickel is very small) are warmed half an hour on a water bath, with an equal volume of concentrated hydrochloric acid, shaking frequently; after filtering through a moistened filter, the filtrate is evaporated in a porcelain dish.

The residue gives (Fortin, *Chem. Ztg.*, 36, 1461 (1912)), when nickel is present, on touching with a drop of 1 per cent. alcoholic dimethyl glyoxime solution, a red coloration, which becomes more pronounced when ammonia solution is added. If the acid extract is itself coloured, it must be boiled with animal charcoal, and filtered.

Kerr (*Journ. Ind. and Eng. Chem.*, 1914, 207) uses 10-20 gm. of hardened fat, dissolves the ash in HCl, evaporates to dryness, and ignites to free from organic matter, transfers to a tall 50 c.c. cylinder, and moistens with a few c.c. of distilled water. Then 50 c.c. of standard dimethyl glyoxime (5 gm. dissolved in 50 c.c. absolute alcohol, and made up to 100 c.c. with concentrated aqueous ammonia, and kept in well-stoppered bottle) are added. The presence of nickel is shown by a red coloration or precipitate. The tint is compared with that produced under same conditions with a nickel solution of known strength.

Edible fat must not contain more than 0·05 mg. of nickel per kilo.

The introduction of hardened fats has rendered doubtful of interpretation many of the standard tests used for specific oils.

The following points are of importance in this connection:—

1. **The Iodine Value.**—This is the most important value, as it gives the degree of hydrogenation of the oils. For methods of carrying out, see under *Analysis of Oils*.

2. The distinctive aromatic alcohols, *Phytosterol* and *Cholesterol*, are *unaffected by hydrogenation*, so that after hydrogenation it is still possible to ascertain whether an oil is of animal or vegetable origin. (See under *Analysis of Oils.*)

3. Most of the tests for individual oils are destroyed, because the process of hydrogenation destroys the substances giving rise to these tests. Thus the *Baudouin Test* for Sesame Oil (red colour when oil is shaken with cold hydrochloric acid and sugar) is rendered almost useless. The same applies to the *Halphen Test* for *Cotton-seed Oil* (orange-red coloration when oil is heated with an equal volume of amyl alcohol and carbon disulphide (1 : 1), the latter containing 1 per cent. free sulphur). The test is rendered more sensitive if *pyridine* is substituted for amyl alcohol, and a closed tube used for the test. (See Gastaldi, *Chem. Zeit.*, 1912, 2, 758.)

4 **Hardened Fish Oils and Whale Oil** are said to contain arachidic and behenic acids—which are the characteristic acids of *Arachis Oil.* Hence an oil adulterated with hydrogenated fish oils would be difficult to distinguish from Arachis Oil by the *Bellier Test* (fractionating the lead salts of the fatty acids by treating with 70 per cent. alcohol).

5. The process of hydrogenation does not affect to any great extent the *saponification value* of the oils thus treated. The *Acetyl value,* however, is usually lowered, owing to the splitting off of hydroxyl groups (Normann and Hügel, *Chem. Zeit.*, 1913, 37815). Thus it would be difficult to detect castor oil when fully hydrogenated by the saponification value and acetyl value.

Costs of Hardening Oils

The following figures refer to the **Costs of Hardening Oils** by the process worked by Norsk Hyderings Co. The figures are the working costs at the works of Centra A.G., Krischwitz, Elbe, and refer to the pre-war conditions (1914).

Actual Cost of Plant required for a Production of 16,000 Tons Hardened Fat per Annum—300 Working Days.

The plant consists of an independent factory. The hydrogen is produced by electrolysis. The necessary electric power (1,000 K.W.) is generated at the factory by means of steam turbines. The exhaust steam is used for heating.

	Austrian Crowns.
(*a*) Complete power plant for 1,300 K.W., consisting of boiler, water purifier, boiler feeding, turbo-generators, condensers, return coolers, including buildings (120,000) and chimney ready for use	530,000
(*b*) Complete hydrogen plant for producing 180 cub. m. hydrogen and 90 cub. m. oxygen per hour with switches, gasometer, oxygen compressor, and all accessories, without flasks, ready for use, including buildings (80,000)	430,000
(*c*) Transport, emptying, storing, and refining of the oils	150,000
(*d*) Hardening apparatuses, complete, ready for use	600,000
(*e*) Buildings (excluding *a* and *b*)	220,000
(*f*) Sundries (rails, etc.)	70,000
	2,000,000

Requisites for a Production of 16,000 Tons Hardened Fat in 7,000 Working Hours, or 2.3 Tons Fat per Hour, according to the Actual Results at Krischwitz.

"Centra"

App. 150 H.P. motor power.
,, 15 men's labour per shift for the hardening.
,, 20 men's labour per shift for the ordinary work.
,, 180 cub. m. hydrogen per hour.
,, 3,000 kg. steam per hour (chiefly for distilled water, if condensed water is not available).
,, 150 kg. coal per hour (for other purposes than power and steam).

Normal Factory.

For 100 kg. hard fat the prime cost is as follows :—	Francs.
6.6 H.P. hours at 4 cent.	0.264
1.5 working hours at 50 cent.	0.750
130 kilos steam at 4 cent.	0.520
6.6 kilos coal at 25 cent.	0.164
	1.7
Wages (francs, 45,000 per annum)	0.28
Chemicals	0.80
Unforeseen	0.22
	3.0

Exclusive of hydrogen, writing off, and interest.

Profit, 100 per cent.—On the basis of whale oil. If inferior qualities are used, the profit will be less; but as the raw material is cheaper, the finished product is of somewhat less value, so that it comes to the same in the end. In calculating, the results will be the same.

Production—16,000 tons hardened fat per annum—7,000 working hours.
Coal—25 francs per ton.
Labour—2,000 francs per annum.
Plant—2,000,000 francs, 1,440,000 francs, 1,040,000 francs.

		Per Annum. Francs.	
Coal—For steam, chiefly for distilled water, if no condensed water is available. For 100 kg. fat, 130 kg. steam are necessary = 20.7 kg. coal—in all, 3,300 tons at 25 francs		82,500	5.20
Coal—For heating, etc., other than power and steam. For 100 kg. fat, 6.6 kg., or 66 kg. per ton—in all, 1,060 tons at 25 francs		26,500	1.66
Chemicals—Fr. 0.80 per 100 kg.		128,000	8.00
Wages—Hardening, 15 men per shift, 30 men at 2,000	60,000		
Other work, 30 men at 2,000	60 000		
		120,000	7.50
Salaries—Office staff, etc.		45,000	2.82
Unforeseen		35,000	2.20
		437,000	27.38
Power—For motors, 150 H.P., 7,000 hours at 4 cent. = 150 × 7,000 0.04		42,000	2.62
		479,000	30.00
Power—For electrolysis, 5 K.W. hr. at 5.45 cent. per cub. m. H_2—8 cub. m. H_2 per 100 kg. fat—in all, 5 × 0.0545 × 80 × 16,000		348,000	21.70
		827,000	51.70
Writing off and interest, 15 per cent. on 2,000,000		300,000	18.80
		1,127,000	70.50
Selling Expenses—3 per cent. of 16,000 francs = 3 per cent. of 12,800,000		375,000	24.00
		1,502,000	94.50

London Oil and Fat Prices in Shillings per 100 Kilos.

Time.	Lin-seed.	Rape Seed.	Cotton.	Soja.	Fish.	Rizinus.	Tallow.
June 1913	55	64	66	57	34	63	73·90
November	50	66	68	57	38	60	74·86
April 1914	57	71	68	57	39	57	73·81
December	50	69	57	49	33	58	70·86
August 1915	55	79	62	46	36	86	72·84
September	57	77	60	47	36	86	74·84
	324 : 6	426 : 6	381 : 6	313 : 6	216 : 6	410 : 6	436 + 511 : 6
	54	71	63.5	52	36	68.2	73·85.6
							79

It will be seen that oils were in 1914, 1915 to be had on the London market at 20·40 shillings per 100 kilos cheaper than the cheapest tallow used for technical purposes.

CHAPTER X

Varieties of Fats, Fatty Oils, and Waxes

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VARIETIES OF FATS, FATTY OILS, AND WAXES

Classification

FOR convenient description we divide the oils and fats under the headings: (1) Animal fats and oils, (2) Vegetable fats and oils, (3) Waxes.

1. **Animal Fats and Oils.** These include **Fish Oils.**—The oils derived from marine animals are characterised by their odours and, analytically, by a high Maumené and iodine value.

2. **Vegetable Fats and Oils** may be conveniently arranged, according to their iodine values, into (*a*) **Solid fats**, (*b*) **Non-drying oils**, (*c*) **Semi-drying oils**, (*d*) **Drying oils**.

No rigid line can be drawn between these classes, as they merge into each other. The iodine value affords a means of ascertaining roughly their constitution and gives a rough basis of classification. Triolein has an iodine value of 86.2, and consequently if an oil absorbs more than 86.2 per cent. of iodine it probably contains the glyceride of an acid of the linolic or linolenic series. Now linolic and linolenic acids and their glycerides readily absorb oxygen from the air—a property not possessed by oleic acid and triolein—and it is due to the presence of **trilinolin** and **trilinolenin** that the drying oils owe their property of drying by absorbing of oxygen on exposure to air. Since the iodine value of pure trilinolin is 173.6, oils having an iodine value of above 170 may be classified as **drying oils**; those having an **iodine value** of 90 or lower may be called **non-drying oils**; while oils having intermediate iodine values may be called **semi-drying**. In practice it is found that **oils** with iodine values above **140** have valuable drying properties; those with iodine values 100-140 are semi-drying, since they are able to absorb a certain quantity of oxygen, but will not dry completely when exposed to the air in a thin layer. Oils with iodine values less than 100 are practically without drying value.

The **Fish oils** form an exception to this rule; some of them have iodine values as high as that of linseed oil and absorb large quantities of oxygen; yet they do not usually dry to a hard layer. Their unsaturated acids are of a different constitution from linolic and linolenic acids.

3. **The Solid Waxes of Animal and Vegetable Origin,** and the liquid waxes (sperm oil, bottlenose oil) are characterised by their high content of higher alcohols (unsaponifiable matter). They do not contain glycerol. They are therefore treated as a separate class under the title of **Waxes** (see p. 139).

Varieties of Animal Fats and Fatty Oils

Tallow, the solid fat of oxen and sheep, consists of tristearin, tripalmitin, and 40-46 per cent. triolein.[1] Mutton tallow melts, 45°-55°; oxen tallow, 45°-50° C.;

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[1] Recent researches have shown the presence of mixed glycerides.

solid point, 40°-47°; Reichert value, 0.25; Hehner value, 96; iodine value, 35-46; saponification value, 193-198; sp. gr. 0.86 at 100°, 0.94-0.95 at 15°. Melting point of fatty acids, 38°-49° C.; solid point, 38°-48°.

Tallow Oil.—Very similar constants to lard oil; iod. val. = 32.57; Maumené, 41°-44° C.

Lard is the rendered fat of pigs. American lard often contains cotton-seed oil and tallow. M.P. 30°-49°; sol. pt. 23°-30°; sap. val. 195-197; iod. val. 50-77; Hehner val. 95-98; sp. gr. (100° C.) 0.860-0.864. The separated fatty acids have sol. pt. 34°-42°; mol. wt. 278; iod. val. 64; refract. index, 1.439 (60° C.).

Lard Oil, Oleo Oil.—Acid val. 0.4; sap. val. 193; Hehner val. 97.4; Reichert-Meissl val. 0.4-0.9; iod. val. 53-88. Insol. fatty acids have sap. val. = 206.

Goose Fat.—M.P. 25°-34°; sol. pt. 18°-20°; sap. val. 184-198; iod. val. 60-72; Reichert-Meissl val. 0.2-0.3; Hehner val. 92-96; sp. gr. 0.91-0.93.

Butter Fat is described under **Butter.**

Bone Fat, from fresh bones.—M.P. 21°-22°; sol. pt. 15°-17° C.; sap. val. 190-195; iod. val. 46-56; sp. gr. 0.914-0.916 at 15° C. **Mixed fatty acids,** M.P. 30°; sol. pt. 28°; neut. val. 200; iod. val. 56-58. Fat extracted from old bones by benzine is dark, smells unpleasantly, contains calcium soap (derived from mineral matter of bones) and free fatty acids. Used for soap making.

Sheep's-foot Oil, Horse foot Oil, and Neat's-foot Oil are yellowish oils valuable for lubricating (since they do not easily become rancid), obtained by boiling the feet of cattle with water.—Sp. gr. 0.91-0.92 at 15° C.; sap. val. 194-197; iod. val. 73-75; Maumené test, 38°-50° C. Mixed fatty acids, sol. pt. 20°-26° C.; iod. val. 66-76; neut. val. 200-206.

Horse Fat, yellowish, often becomes rancid.—Sp. gr. 0.90-0.93 at 15° C.; 0.79-80 at 100° C.; M.P. 40°-50°; sol. pt. 22°-48°; iod. val. 75-85; Reichert val. 0.33; Hehner val. 95. Mixed fatty acids, M.P. 36°-41°; sol. pt. 30°-33°; iod. val. 74-84.

Fish Oils are usually fluid, containing glycerides of oleic, stearic, physetolic acids, and other unsaturated acids. Unless of the best medicinal qualities these oils are dark, evil-smelling fluids in consequence of small quantities of decomposition products of decaying fish (trimethylamine).—Sp. gr. 0.92-0.93; sap. val. 170-200; iod. val. 100-110; Reichert val. 1.5-2.2; Hehner val. 95; Maumené's test, 100°-128° C. Mixed fatty acids, sol. pt. 21°-28°.

Fish oils are now used both in the ordinary and in the enamel leather trade with excellent results; and the enamel leather produced, whilst not quite so glossy as when linseed oil is used, is said to be more flexible and less liable to crack; also for soap-making, and in the manufacture of printing ink.

When cooled, fish oils often deposit solid masses of **Fish stearin** (fish tallow).

Sod Oil (Dégras) is the waste oil obtained in the process of chamoising leather. The leather is soaked in fish oils and then exposed to the air. Oxidative and fermentative processes set in which convert the contained oil into sod oil. The oil is extracted from the leather by means of sodium carbonate solution, and then separated from the emulsion it thus forms by the addition of dilute sulphuric acid. A similar product is obtained by blowing air through fish oils heated to 120° C. Sod oil consists principally of unchanged fish oil, owing its valuable properties to the presence of a resinous acid, "dégras former," of unknown constitution, soluble in alkalis, insoluble in petroleum ether; it is this substance which makes sod oil so suitable for oiling dressed leather.—Sp. gr. 0.92-0.98 at 15° C.; refract. index, 1.475-1.478; acid val. 8-28; sap. val. 180-190 (from shark-liver oil only, 143); acetyl val. 22-48; iod. val. 70-100.

Varieties of Vegetable Fats and Oils

(*a*) Solid Vegetable Fats (*i.e.*, M.P. above 20° C.)

Cacao Butter is expressed from cacao beans in the process of working them into cacao.—M.P. 30°-34°; sap. val. 192-200; iod. val. 34-37; Reichert-Meissl val. 0.83; refract. index (60° C.), 1.45. Sp. gr. 0.96-0.97 at 15°, 0.85-0.86 at 100°. The insol. acids have M.P. 48°-53°; neut. val. 190; iod. val. 32-39; refract. index, 1.42 (60° C.).

The main use of cacao butter is for making chocolates. It has also a considerable value as a cosmetic (face pomade), and large quantities are used by pharmaceutical chemists as a media for conveying drugs, etc., into the skin. In certain diseases of the nose, female genital organs, etc., solid blocks of cacao butter impregnated with antiseptics are introduced as a convenient method of treating the affected parts.

The author, in conjunction with Mr J. W. Brizell, worked out (English Patent, 123,231, 1918) a method of deodorising cacao butter (1918). They discovered that the flavouring and scenty matter is volatile, and by heating the substance to 140° C. and blowing steam through for a few minutes both the yellow colour and taste can be removed and a pure white fat is left. Simply heating or passing an indifferent gas through has the same effect.

Cacao butter is also an excellent fat for cooking, as the author showed (see his pamphlet, "Cocoa Butter for Cooking Purposes," published by the Co-operative Wholesale Society, Ltd., Stationery Department, Manchester). For ordinary domestic cooking half quantities of fat should be used, compared to the quantity of lard ordinarily used for cooking. Full details of use are given in above pamphlet.

Chocolate Fats.—The best substitutes for cacao butter are made by expressing, at a temperature slightly over the normal atmospheric temperature, the solid fats which crystallise out from palm-nut and coco-nut oils. Small quantities of animal fats are sometimes added to raise their melting points; these, however, sometimes impart an unpleasant taste, and it is better to use for the purpose vegetable fats such as those from margosa or mowra oil. Sap. val. 242-254; iod. val. 6-10; M.P. 25°-30°; Reichert-Meissl, 3.5-8.0. Hardened oils are also used.

Nutmeg Butter is obtained from the seeds of *Myristica officinalis*.—Sp. gr. 0.94-99 at 15°, 0.88-90 at 100°; M.P. 38°-50° C.; acid val. 22; sap. val. 156; iod. val. 40-80.

Chinese Vegetable Tallow is the hard fat which coats the seeds of the Chinese tallow tree.—M.P. 44°-53° C.; sap. val. 200; iod. val. 32.

Japan Tallow is a similar fat which surrounds the berries of certain sumach trees which flourish in China and Japan; rich in palmitin.—M.P. 50°-53°; sap. val. 220; iod. val. 4-15.

Palm Oil, obtained in very large quantities from the fleshy parts of the fruit of certain palm trees, is a fat having a sweetish taste and an odour resembling that of violets, which persists even after bleaching with air at high temperatures, and after making into soap. It consists principally of tripalmitin, triolein, and free fatty acids; the proportion of the latter is sometimes very large in commercial specimens owing to a process of enzyme hydrolysis which goes on in the shipped oil.—Sp. gr. 0.92 at 15° C., 0.85 at 100° C.; sol. pt. 31°-38°; M.P. 27°-42° C.; sap. val. 202; iod. val. 51-57; Reichert-Meissl val. 0.9; Hehner val. 95; refract. index (60° C.), 1.451. Insol. fatty acids have sol. pt. 36°-45°; M.P. 47°-50°; neut. val. 204-206; iod. val. 53. For manufacture see p. 58.

Palm-kernel Oil, Palm-nut Oil is obtained from the kernels of the palm tree fruit, and contains much lauric acid. It is easily saponified by cold concentrated caustic soda solution.—Sp. gr. 0.91 at 15°, 0.87 at 100° C.; sol. pt. 23° C.; M.P. 23°-30° C.; sap. val. 250; iod. val. 10-17; Reichert-Meissl val. 5-7; Hehner val. 251-265; iod. val. 12. For manufacture see p. 58, and for merchantable standards see p. 196

Coco-nut Oil is the fat obtained from the kernels of the coco-nut. The fleshy part of the kernel, called copra, contains a large amount of fat, which consists of glycerides of lauric, myristic, palmitic, and other acids, some of them volatile. The fat, like palm-kernel oil, is easily saponifiable in the cold by concentrated caustic soda solution. Largely used for soap and margarine manufacture. For the latter purpose it is deodorised (1) by washing with alcohol, or (2) by treating with superheated steam (see pp. 79, 89).—Sp. gr. 0.92 at 15°, 0.86-0.90 at 100° C.; sol. pt. 16°-23° C.; M.P. 23°-26°; sap. val. 250-260; iod. val. 8-9; Reichert-Meissl val. 7.8; refract. index, 1.43 (60° C.). The fatty acids have sol. pt. 20°-25°; neut. val. 258; iod. val. 8-9. For manufacture see p. 59, and for merchantable standards see p. 196.

Mahwa Butter, Mohwrah Butter, Mohrah-seed Oil (from *Bassia latifolia*).—M.P. 23°-29°; acid val. 5-71; sap. val. 187-194; Hehner val. 95; Reichert-Meissl val. 0.4-1.0; iod. val. 50-68. Insol. fatty acids, sap. val. 206.

Mowrah-seed Oil (from *Bassia longifolia*).—Sap. val. 196-202; iod. val. 50.

Myrtle Wax.—Acid val. 3; sap. val. 205-212; iod. val. 1.9-4. **Fatty acids** have neut. val. 230.

Shea Butter, Bambuk Butter, Karité Oil, from the seeds of *Bassia Parki* (West Africa and Soudan).—Sp. gr. 0.85-0.92 (15° C.); M.P. 25°-28° C.; sol. pt. 17°-18°; sap. val. 171-192; iod. val. 56-59.

(*b*) LIQUID VEGETABLE NON-DRYING OILS.

These do not absorb oxygen from the air, nor do they dry up. Iodine value usually under 100.

Olive Oil, much valued as an edible oil (salad oil), is obtained from the fruit of the olive tree. The cold pressed oil is the best; the second pressing, or the oil extracted by carbon disulphide, is used for soap-making; consists of 70 per cent. triolein, 28 per cent. tripalmitin and tristearin, and a little linolein.—Sp. gr. 0.914-0.918; sol. pt. 2°-4° C.; sap. val. 190-195; iod. val. 79-93; Reichert-Meissl val. 0.6; Hehner val. 95; Maumené test, 41°-47° C.; refract. index, 1.47 (15° C.); viscosity, 312 secs. at 21° C. The fatty acids have sol. pt. 17°-26°; neut. val. 193; iod. val. 86-90. For manufacture see p. 57.

Olive-kernel Oil.—Acid val. 2-3.5; sap. val. 182-188; iod. val. 79-88.

Almond Oil, obtained from bitter and sweet almonds, is very similar to **Peach-kernel Oil, Plum-kernel Oil,** etc.—Sap. val. 190-195; iod. val. 93-100.

Arachis Oil (Pea-nut, Earth-nut, Ground-nut) is an edible oil obtained from the seeds of *Arachis hypogæa*. It contains arachidic acid as a glyceride.—Sap. val. 190-196; iod. val. 90-103; Reichert-Meissl val. 0.5; Maumené, 45°-75°; viscosity, 300-430 secs. at 21° C.; refract. index (15° C.), 1.147. The insol. fatty acids have sol. pt. 23°-28°; neut. val. 202; iod. val. 96-105. For standards of merchantable value see p. 196.

Croton Oil.—Sap. val. 210-215; Reichert-Meissl val. 12-14; acetyl val. 38-41; iod. val. 101-109; sol. pt. 7° C. **Fatty acids** have neut. val. 201 and iod. val. 111-112.

Grape-seed Oil.—Acid val. 16; sap. val. 178-179; Reichert-Meissl val. 0.46-2.0; iod. val. 94-97. **Fatty acids** have neut. val. 187 and iod. val. 98-100.

Castor Oil, obtained principally from the seeds of *Ricinus communis*, consists mainly of the glyceride of ricinoleic, isoricinoleic, and dihydroxystearic acid, together with a little tristearin. It is a very viscous oil, miscible with absolute alcohol and glacial acetic acid in every proportion, and much used as a medicine and lubricant, but also for manufacturing Turkey red oils (which see).—Sp. gr. 0.960-0.966 (15° C.); sol. pt. −10° to −12° C.; sap. val. 176-183; iod. val. 83-86; refract. index, 1.480 (15° C.); viscosity, 1,160 secs. at 37° C.; Reichert-Meissl val. 1.1. Mixed fatty acids, M.P. 13° C.; Maumené, 47. For manufacture see p. 56, and for merchantable standards see p. 196.

Blown Oils, Oxidised Oils, Soluble Castor Oils.—When semi-drying vegetable oils, blubber oils, and liquid waxes are placed in a vessel provided with a steam heating coil, and warmed from 70°-115° C., while a current of air is blown through, the oils oxidise to viscid, dense fluids which are miscible with mineral oils. They form valuable lubricating oils, approaching castor oil in mechanical properties; since castor oil is insoluble in mineral oils (and so cannot be mixed with them), such oils are known commercially as "**Soluble Castor Oils.**"

Turkey Red Oils, Sulphonated Oils are viscous, transparent liquids used in the preparation of cotton fibre for dyeing and printing Turkey red. Concentrated sulphuric acid is slowly run, with constant stirring, into castor oil, the temperature being kept below 35° C. during the whole course of the reaction. The product is washed with water, settled, the lower layer drawn off and washed with a solution of Glauber's salt until only slightly acid; finally ammonia or soda is added until the sample will give a complete emulsion with water. Turkey red oil F. is completely soluble in water. Turkey red oil S. is only partially soluble in water.

Nitrated Oils are heavy, viscid liquids obtained by treating castor (or linseed) oil with a mixture of 2 parts of concentrated sulphuric acid and 1 part of concentrated nitric acid (sp. gr. 1.5). They form homogeneous mixtures with nitro-cellulose. Thus a product resembling ebonite is obtained by mixing 1 part of nitrated castor oil with 9 parts of nitro-cellulose. Dissolved in acetone, these nitrated oils form varnishes which are capable of enamelling leather and mixing paints.

Bone Tar or Bone Oil is the dark evil-smelling liquid formed during the dry distillation of bones in the preparation of bone black (animal charcoal). It contains considerable amounts of pyridine and quinoline, their homologues and other bases. These compounds may be extracted from it by the use of sulphuric acid. For details see Martin's "Industrial Chemistry: Organic," p. 420.

(c) SEMI-DRYING VEGETABLE OILS.

These absorb oxygen from the air and become thick, without, however, completely drying up. Iodine value from 95-140.

Cotton-seed Oil is produced on an enormous scale in North America from the seeds of the various sorts of cotton trees; 17,000 tons, of value £580,000, were imported into Britain in 1910. It consists of glycerides of palmitic, oleic, and various unsaturated and hydroxy acids which cause the oil to somewhat rapidly oxidise at ordinary temperatures. It is, therefore, a weak drying oil. When cooled it deposits a large amount of cotton-seed stearin. Used as an edible oil, for adulterating lard, in the manufacture of margarine, soap, and lubricants.—Sp. gr. (15° C.) 0.922-0.930; sol. pt. 3°-4° C.; sap. val. 191-195; iod. val. 105; refract. index, 1.478 (15° C.); Maumené, 74°-78° C. Fatty acids have M.P. 35°-38°; neut. val. 201-208; iod. val. 110-115. For manufacture see p. 55, and for standards of quality see p. 196.

Test for Cotton-seed Oil.—Dissolve 5 c.c. of the fatty acids from the oil in 2 c.c. alcohol in a test tube. Heat to boiling on water bath; add 2 c.c. of $2N.AgNO_3$ solution; an immediate black colour shows presence of cotton-seed oil. Five per cent. of cotton-seed oil can be detected in rape or olive oil by this test.

Rape or Colza Oil, Sweet Oil, obtained from the seeds of *Brassica campestris*, contains considerable quantities of rapic acid, $C_{17}H_{32}.OH.COOH$, and other unsaturated oxy-acids. Being cheap, it is much used for lubricating and edible purposes. The pure oil on exposure to air remains fluid for some days, but long exposure causes it to thicken somewhat and become rancid. If adulterated with drying oils it rapidly turns into a jelly like mass, or even becomes solid.—Sp. gr. 0.914-0.918; sap. val. 170-178; iod. val. 94-107; Hehner val. 95; Reichert-Meissl val. 1 c.c.; viscosity, 330-380 secs. at 21° C., 91-94 secs. at 60° C.; Maumené test, 60° C. The elaidin test is here very useful for detecting presence of drying oils in rape oil. The fatty acids have sol. pt. 13°-18°; neut. val. 185; iod. val. 96-104. See also p. 61, and for merchantable standards see p. 196.

Sesamé Oil, obtained from the seeds of the sesamé plant, *Sesamum indicum* and *orientale*, is a valuable edible oil consisting of a mixture of the glycerides of stearic, palmitic, oleic, and linolic acids. To detect the presence of the oil, dissolve 0.1 g. sugar in 10 c.c. HCl (sp. gr. 1.19); add 20 c.c. of oil; shake and allow to stand: crimson colour in the aqueous filtrate shows presence of sesamé oil.—Sp. gr. (15° C.), 0.914-0.916; sap. val. 188-195; sol. pt. −5° C.; iod. val. 103-112; Maumené, 65°-72° C.; Reichert-Meissl, 0.7 c.c. For merchantable standards see pp. 196, 197.

Sunflower-seed Oil.—Acid val. 0.2-6; sap. val. 190-193; iod. val. 118-136; Maumené, 67°-75° C. Fatty acids have sap. val. 201 and iod. val. 124-134. See p. 61.

Maize Oil, Corn Oil.—Obtained from germs of the maize plant, *Zea Mays*, L. The germs are a by-product in glucose and starch works using maize as their raw material. Acid val. 2-20; sap. val. 187-190; Hehner val. 88-94; Reichert-Meissl val. 0.3-10; iod. val. 113-129. Fatty acids have neut. val. 200 and iod. val. 121-127. For standards of merchantable quality see p. 196.

Pumpkin-seed Oil has acid val. 3.5-19; sap. val. 188-195; iod. val. 104-130.

Black Mustard Oil has acid val. 5-8; sap. val. 173-175; iod. val. 98-119.

White Mustard Oil has acid val. 5-6; sap. val. 170-171; iod. val. 92-96.

Soya Bean Oil, from the seeds of *Dolichos Soja*, L., *Soja hispida*, *Soja japonica*, etc., plants indigenous to Manchuria, Japan, China. The seed contains 18 per cent. oil and 30-40 per cent. protein, and yields 13 per cent. oil. The expressed meal is made into bean-cakes; the soya bean industry being one of the most important of Manchuria and Japan, 1,500,000 tons of oil being exported in 1911. The oil consists of glycerides of oleic and linolic acids, dries on standing to a thin skin, and is used for edible and illuminating purposes in the Far East; now used as a paint and linoleum oil. See Toch, *Jour. Soc. Chem. Ind.*, **31**, 572 (1912).—Sp. gr. 0.924; sap. val. 190-193; iod. val. 121-124; Maumené, 59°-61°; sol. pt. +8°-15° C. The fatty acids have a M.P. 27°-29°; sol. pt. 25°; iod. val. 115-122. See also p. 61, and for standards of merchantable value see p. 196.

(*d*) DRYING VEGETABLE OILS.

These absorb oxygen from the air and dry up to a hard skin. They have an iodine value usually over 140.

Hemp-seed Oil has a sap. val. 190-195 and an iod. val. 140-166; Maumené, 95°-98°. Separated fatty acids have a sol. pt. 14°-16°; iod. val. 122-140.

Candle-nut Oil has a sap. val. 184-193 and an iod. val. 136-163.

Niger-seed Oil has a sap. val. 189-192 and an iod. val. 126-134.

More important than these are the following:—

Poppy-seed Oil, a pale yellowish oil obtained by pressing from seeds of the poppy, is used as a salad oil and for making artists' paints: a good drying oil.—Sp. gr. (15° C.) 0.92-0.97; sap. val. 192-197; iod. val. 137-143; Reichert-Meissl val. 0.0; Hehner val. 95; Maumené test, 88° C.; refract. index, 1.477 (15° C.). Fatty acids have sol. pt. 16.5; neut. val. 199; iod. val. 139; refract. index, 1.451 (15.5° C.). The differentiation of poppy oil from walnut oil—*e.g.*, in the examination of white paints—is achieved most readily by the hexabromide test (which see); walnut oil yields 1.4-2 per cent. of hexabrominated glycerides, poppy-seed oil none See p. 61.

Walnut Oil, a very good but expensive drying oil obtained from the seeds of the common walnut tree; being almost colourless, it is used for making the best white paints for artists, such paints being less liable to crack than those made from linseed oil. For distinction from poppy-seed oil see the latter. It is frequently grossly adulterated with mineral oil.—Sp. gr. 0.925-7 (15° C.); sap. val. 192-198; iod. val. 143-151; Maumené test, 96°-110° C.; Reichert-Meissl val. 0.0; Hehner val. 95. Fatty acids solidify at 16° C., and have iod. val. 150.

Tung Oil, Chinese Wood Oil, Wood Oil, a very important drying oil, possessing a characteristic odour and an even more pronounced drying power than linseed oil (giving, however, a *wax-like*, *non-elastic* product which renders it quite useless for paints in its ordinary condition), and when heated alone in absence of oxygen to 180°-250° C., it polymerises to a solid mass. It is said to be used for adulterating Chinese lacquers, and has been used in a solidified form for linoleum manufacture (see p. 136). In 1906, 28,685 tons were exported from Hankow, while the home consumption in China may amount to 60,000 tons. It is obtained from the seeds of *Aleurites cordata* and other trees growing in China, Japan, Tonkin, Annam, etc. It consists principally of glycerides of *oleic* and *elæomargaric acids*.—Sp. gr. 0.94; sap. val. 190-195; iod. val. 149-167; Maumené, 300°-372°. Separated fatty acids have sol. pt. 31°-37°; neut. val. 189; iod. val. 145-160.

LINSEED OIL AND PRODUCTS DERIVED THEREFROM

Linseed Oil, a yellowish-brown fluid from the seeds of the flax plant, *Linum usitatissimum*, is largely used for paint, varnish, oil-cloth, linoleum, and soft soap manufacture. The oil is principally composed of glycerides of unsaturated acids like isolinolenic acid (58 per cent.), linolenic acid (13 per cent.), linolic acid (13 per cent.), oleic acid (4 per cent.). The oil rapidly absorbs atmospheric oxygen, with formation of a tough resinous mass, and hence is a "drying oil." This drying property is increased by heating to 180° C. or by the addition of metallic salts—"driers"; 38,000 tons, value £1,250,000, were imported into England in 1910. For manufacture of linseed oil see p. 53.

Constants of Linseed Oil.—Sp. gr. (15° C.) 0.93-0.94; sap. val. 190-195; iod. val. 173-193; Reichert-Meissl val. 0.00; Hehner val. 95; Maumené test, 103°-145° C.; refract. index (15° C.), 1.4835; viscosity (21° C.), 212 secs. Flash-point, about 243° C. (470° F.). **Mixed fatty acids** solidify at 13°-17° C.; melt at 17°-24° C.; neut. val. 196-199; and iod. val. 179-200. For quality tests see p. 196.

To test the drying properties of linseed oil, smear a glass plate with the sample and expose in the water oven. Note how long it takes to dry, also the nature of the residuum; compare with a standard sample treated in the same manner.

To find presence of driers incinerate 50 g. in a large porcelain crucible and analyse residue for metals.

To find whether suitable for linoleum-making heat some in a copper basin to 260° C., stirring and blowing air through the mass. Dense fumes are evolved, and after a time it becomes thicker. A specimen is drawn out and cooled. It should be "stringy," *i.e.*, capable of being drawn out into threads. Compare with a standard sample of oil treated similarly. Adulteration with mineral oils lowers the saponification value.

The Chemistry of the Driers.*—The chemical changes taking place when linseed oil "dries" or "sets" are very complex, and, although they have been carefully studied by numerous different investigators, our knowledge of the same is very indefinite and unsatisfactory. We do know, however, that it is the result of oxidation, for the oil may be stored unchanged for an indefinite time *in vacuo*, or in the presence of an inert gas such as nitrogen. When oxygen can gain access to the oil, an increase in weight becomes apparent, and an elastic solid called "linoxyn" is produced, resulting in the "drying" of the oil. The term "drying," however, is misleading, for it implies that water has evaporated, leaving a solid residue—which is not the case.

We are not to suppose that linoxyn is a single substance, or that it is produced by the mere addition of oxygen to the linseed oil molecule. During the process of drying, not only is oxygen absorbed, but formaldehyde, and carbonic and formic acids are simultaneously liberated, showing that very complex reactions are taking place.

It has been known for many years that certain substances can accelerate the setting of linseed oil, and they are therefore known as "driers." The actual way in which these bodies act is obscure. Owing to the fact that some of the most common driers were highly oxygenated bodies, like manganese dioxide (MnO_2) and red lead (Pb_3O_4), a very plausible theory was advanced, according to which the driers themselves gave up to the oil the necessary oxygen to induce setting. When, however, quantitative experiments were performed, and proved that a ton of linseed oil can absorb from 3-5 cwt. of oxygen,† whereas only about 5 lbs. of drier are added to the same weight of oil, it was evident that such a theory was, to say the least, very incomplete. This led to the enunciation of the so-called "catalytic theory of driers," according to which the driers act as catalysers, that is to say, they assist the oil to take up oxygen without themselves undergoing a permanent alteration. The exact way in which this is done is uncertain, but it is usually assumed that when suspended in the oil or paint they unite with the atmospheric oxygen to form unstable, highly oxygenated bodies, which hand over their excess of oxygen to the oil almost immediately, being themselves reduced to their original condition. They are now in a position to unite with more oxygen, and to yield that up again in a precisely similar manner to the oil. And so the process goes on indefinitely until the oil has set.

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* For a more detailed discussion of the action of driers on linseed oil the reader is referred to "An Introduction to the Chemistry of Paints," by J. Newton Friend (Longmans & Co., 1910).

† This is based on the fact that during the process of setting, linseed oil has been observed to absorb from 15-18 per cent. by weight of oxygen gas.

The two main facts that may be cited in favour of this theory are as follows:—

1. A small quantity of drier is able to effect the rapid oxidation of a large amount of oil.

2. The best driers are the oxides or salts of those metals which are known to exist in various stages of oxidation, and to be readily oxidised to, or reduced from one state to another. Thus, for example, manganese, lead, and iron, from which the bulk of the best driers are prepared, each yield a series of well-defined oxides containing varying proportions of oxygen.

In the accompanying table * a list is given of the common driers, together with the percentage of metal usually found in them. The theoretical percentage of metal cannot always be given, as the composition of the finished product varies according to circumstances, the amount of water of crystallisation in particular being dependent upon the temperature at which the salts are prepared.

TABLE OF COMMON DRIERS.

Name.	Colour.	Per Cent. Metal in Pure Drier.	Per Cent. Metal in Commercial Drier.
Litharge	Buff	90.3	89.4
Red lead	Red	90.1	86.7-87.6
Lead acetate	White	54.6	52.4-53.3
,, linoleate	Brown	...	31.2
,, oleate	Yellow		22.6
,, rosinate (fused)	Yellow-brown	..	15.6
,, ,, (ppted.)	Light brown		...
Manganese borate	Pinkish	...	7.8-23.8
,, carbonate	Buff		38.8-42.6
,, dioxide	Black	63.2	50.4-54.3
,, hydroxide	Brown	..	46.5
,, linoleate	Dark brown	..	7.8-8.9
,, oleate	Brown	.	8.1
,, oxalate	Pinkish	.	30.2
,, rosinate (fused)	Dark brown	..	2.3-3.5
,, ,, (ppted.)	Pinkish	...	5.0-6.1
,, sulphate (anhydrous)	Pinkish	36.4	...

As is evident from the above table, a considerable variety of substances are placed under the category of driers. In the case of the metallic salts the efficiency is influenced to a slight extent by the nature of the acids with which the metal is combined. If this latter is favourable to the catalytic action, the drier is slightly more powerful than might otherwise be expected. This is true of rosinic acid, and metallic rosinates have of late found great favour amongst painters generally. They may be prepared by fusing together rosin and a metallic oxide, a product free from moisture being obtained, and known as a "fused" drier. "Precipitated" driers, as their name implies, are obtained by mixing solutions of alkaline rosinates with a soluble metallic salt, whereby the drier is precipitated. Such driers always contain a considerable quantity of moisture, up to, say, 6 per cent., and are

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* This table is taken from Friend's "Introduction to the Chemistry of Paints," p. 155, the data having been calculated from the results given by T. A. Davidson in his paper entitled "The Action of Driers on Linseed Oil," read before the Paint and Varnish Society, 12th November 1908.

thereby readily distinguished from fused driers. Other organic salts, such as the oleates and linoleates of lead and manganese, are also very efficient driers. Lewkowitsch has recently prepared tungates of these metals from the fatty acids of tung oil.

Since these organic compounds are readily soluble in turpentine and linseed oil, they are known as "soluble" driers. Solutions in either or both of these solvents are termed "liquid" driers or terebines.

It does not always follow, however, that the most powerful driers are necessarily the best for all work; other properties should be taken into consideration. For example, lead acetate is well known to be weaker than red lead and litharge, nevertheless it is used extensively in the manufacture of patent driers because it does not darken the oil so much—a point of considerable importance when white and light-coloured pigments are being used. Ferrous sulphate should be used with care as it tends to render the film of oil brittle.

Now, according to the catalytic theory, chemically inert substances cannot be expected to function as driers. Nevertheless Hurst [*] found one "patent" drier to contain more than half its weight of calcium sulphate, whilst another contained 77 per cent. of barium sulphate (barytes) and silica. It would be unwise, with our present limited knowledge, to assume that chemically inert bodies are necessarily useless as driers, for it may well happen that the introduction of fine particles of solid into the oil can assist in some physical manner the absorption of oxygen, just as we know fine powders can greatly accelerate the oxidation of combustible gases. At present the only method of determining whether or not a drier is of any value is to test it experimentally in some such manner as that indicated below.

Turpentine is not infrequently regarded as a drier, but the researches of W. N. Hartley would seem to indicate that such is not the case in the strictest sense of the term. Turpentine assists in the drying of the oil by rendering it thinner, so that the painter can spread it over a larger surface, and thus come into contact with a proportionately greater quantity of air. It is not impossible, however, that whilst the above is the main function of the turpentine, a catalytic action does take place to a small extent in addition, for it is well known that turpentine readily absorbs oxygen from the air, yielding, as many chemists believe, an organic peroxide, which latter would act on the oil in an analogous manner to an inorganic peroxide.

In the case of litharge and red lead, complications arise owing to the tendency which these oxides exhibit to saponify the oil, whereby an insoluble lead soap is produced, which produces a more brilliant coat on drying than the pure oil alone. To what extent this saponification assists the rate of drying is at present unknown.

Practical Testing of Driers.[†]—The old method of testing driers by noting the time taken by a thin film of terebine to set hard on glass cannot be too strongly condemned, for it leads to most conflicting results. One of the most satisfactory methods is that given by T. A. Davidson.[‡] This investigator prepares a series of mixtures of linseed oil and drier in varying proportions. These are kept at a uniform temperature for a number of hours in separate stoppered bottles. The liquids are now filtered through paper into fresh bottles, and a portion of each is run on to a glass slide and placed in an air oven at constant temperature. From time to time the slides are examined and the number of minutes or hours noted that are required before the film is sufficiently firm to bear the finger being gently drawn across it without leaving a whitish mark. This time is known as the "setting value," and is greatly affected by a number of factors, such as temperature, rate of change of air, thickness of the oil film, moisture, and the nature of the surface to which the oil is applied. In testing a drier, therefore, it is necessary to perform two series of experiments at the same time and under precisely similar conditions, one with a standard drier, whose efficiency is well known from practical experience; the other with the sample to be tested. Only in this way is it possible to arrive at satisfactory and reliable results.

Varnishes, Lacquers, and Enamels

Varnishes, lacquers, and enamels, when applied to the surfaces of bodies, have in general two functions to fulfil, namely, those of protection and of ornamentation.

Oil Varnishes were first manufactured on a commercial scale in England at the close of the eighteenth century, and are prepared by dissolving resins in linseed oil. Owing to the fact that the resins are, as a rule, insoluble in the oil beforfusion, varnishes cannot be prepared by simply mixing the ingredients at the temperature of the room. The resins are first fused in copper gum pots, and a quantity of oil already at 500° F. (260° C.) is added under vigorous stirring. The contents of the pot are now run into a large iron tank capable of holding the "runnings" of several pots, and the temperature maintained at 500° F. until the varnish has cleared and is stringy. It is then cooled, thinned with turpentine, and stored to clear and age.

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[*] See "Painters' Colours, Oils, and Varnishes," by Geo. Hurst (Griffin & Co., 1906), p. 437.

[†] This subject is dealt with in further detail in Friend's "Introduction," etc., p. 161 *et seq.*

[‡] Davidson, *loc. cit.*

Simple as the above process appears to be in theory, years of practice are required to produce thoroughly satisfactory results. If the resin is not properly fused it cannot undergo thorough union with the oil, the imperfectly fused portions remaining suspended as very fine insoluble particles in the varnish, instead of being dissolved in the same. The result is that when the varnish is applied to any surface it sets with a "bloom." Whilst this is not the only cause of blooming it is a sufficiently common one to merit attention.

For pale varnishes it is essential that the resins employed be pale, and, unless the temperature of the gum pot is carefully watched and maintained as low as possible, the resins will darken and spoil.

These technical difficulties, coupled with the fact that the already costly resins lose from 5-20 per cent. in weight during fusion, have led to many attempts on the part of manufacturers to employ some other method. Experiments have been carried out with terpineol, with amyl alcohol, and with naphthalene and phenols as solvents, but with doubtful success.

Enamels consist of oil varnishes into which certain finely levigated pigments, such as zinc oxide and venetian red, have been thoroughly ground. Black enamels are usually prepared from asphaltum.

Spirit Varnishes are prepared by mixing resins with such solvents as methylated spirit or turpentine, and allowing to stand in a warm place. Excessive heat must be avoided, owing to the volatile nature of the solvents, and the inflammability of their vapours. The methylated spirit employed should not be weaker than 64 over proof.

Nitro-cellulose Varnishes.—Varnishes used in the manufacture of artificial leather and in special lacquer work consist of nitro-celluloses dissolved in amyl acetate and suitably coloured. About 450,000 gallons of amyl acetate are annually employed in the United States for making such nitro-cellulose varnishes. These varnishes are likewise used for painting iron work owing to their non-porous nature.

Water Varnishes are made by dissolving gums or glue in water. If, just before use, a small quantity of potassium bichromate is added to glue varnish, the coat is rendered almost waterproof.

Natural Varnishes.—Two genera of plants belonging to the *Anacardiaceæ* yield a sap on tapping, which is used in the Far East as a natural varnish or lacquer, namely, *Rhus* for Japanese and Chinese lacquers, and *Melanorrhea*, which yields black Burmese varnish. Japanese lacquer is hard, its hardness increasing with age. Its great value lies in its persistent lustre, and to the resistance which it offers to such agencies as spoil our ordinary oil varnishes. It should be borne in mind that the so-called lac ware of India is not true lacquer ware, as it is produced by the aid of shellac dissolved in suitable liquid menstrua. The chief Chinese tree yielding lacquer is *Rhus vernicifera*, native to that country, and, like the art of lacquering, introduced from China into Japan. Chinese lacquer is frequently adulterated with tung oil. When first obtained from the tree it is greyish white in hue, but quickly oxidises and becomes brownish black. The Japanese lacquer is very similar. Both lacquers harden only in a moist atmosphere, hence in China lacquering is performed in wet weather, and in Japan it is conducted in special moisture-laden rooms. Oxygen is slowly absorbed during the setting to the extent of 5.75 per cent. of the weight of the original varnish. The only methods of thinning the lacquer known to the Japanese are by warming, or by addition of camphor. For this reason camphor wood is not used as the foundation for lacquer, although almost any other kind of wood may be employed.

Solidified Linseed Oil, Linoxyn, Oil Cloth, and Linoleum

LITERATURE

See REID, *Journ. Chem. Soc. Ind.*, 1896, 75.
INGLE, *loc. cit.*, 1904, 1197.
A. DE WAELE and O. J. PATRICK, "Linoleum: Its Manufacture and Valuation," *loc. cit.*, 1915.

The technical literature is poor, and much of the materials for the accompanying article were privately communicated by firms interested in the trade.

Linseed oil rapidly takes up oxygen and solidifies to a flexible solid mass of unknown constitution, termed "solidified linseed oil," "oxidised linseed oil," "linoxyn," etc. The substance is manufactured on a large scale by several different processes (F. Walton, 1860-63).

1. Linseed oil, freed from moisture by settling (sometimes by filtering through dry salt)—otherwise frothing ensues on boiling—and boiled with a drier to accelerate oxygen absorption, is allowed to flow down a light cotton fabric ("scrim") suspended from the ceiling of a high room which is maintained at 38° C. The flooding with oil takes place daily, and each layer solidifies in about twenty-four hours. The process is continued for six to eight weeks, the oil dripping from the cloth being drawn off and allowed to flow again down the cloth. When the layer of solidified linseed oil is half an inch thick, the "skins" (25 ft. long) are cut down, and the mass passed between rollers. It is known as "scrim oil." The scrim at first supports the oil, but before the skins are ready to be cut down the cotton is so thoroughly rotted that it readily disintegrates, and cannot be traced in the subsequent processes through which the oil passes.

2. Raw linseed oil is placed in a horizontal steam-jacketed cylinder within which a central shaft provided with arms rotates with high velocity. The cylinder is only half filled with oil, and the arms beat it up into a fine spray, while at the same time a current of air is driven through. Steam in the jacket is maintained so as to heat the oil to a proper temperature (which differs with the kind of oil to be produced). As the oxidation proceeds the temperature rises, and the steam is now replaced by cold water. The oil is oxidised in five to six hours, but if an oil of a light colour is required, twenty-four hours is required. The thick viscous liquid is run while hot into trays, where it solidifies on cooling. At this stage it is not so thoroughly oxidised as "scrim" oil, and (except when used for cork carpet) the trays have to be kept in stoves at a temperature of about 38° C. for from four to eight days until the desired degree of oxidation is obtained.

In this forced method of oxidation there is a loss of about 8 per cent., whereas in the natural oxidation of the "scrim" method there is an actual gain of about 7 per cent. The oil oxidised in this manner is more liable to spontaneously ignite than that produced by the "scrim" process. The oil is not quite so elastic as that prepared by the "scrim" process, owing to part of the oxidised oil being "superoxidised" to a liquid substance, first discovered by Reid.

3. A third process for reducing linseed oil to a thick mass suitable for mixing with ground cork, etc., for linoleum making is achieved by prolonged boiling alone, which causes the oil to polymerise. A considerable proportion of the linoleum sold at the present day is made from oil so prepared. The manufacture of linoleum from polymerised linseed and tung oil has been patented by Dewar and the Linoleum Manufacturing Company (English Patent, 5,789, 1903).

LINOLEUM AND OIL-CLOTH MANUFACTURE.*

The first step in the manufacture of linoleum is the production of "linoleum cement." This is done by melting the solidified oil with various gum resins

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* See Reid, *Journ. Soc. Chem. Ind.*, 1896, 75; Ingle, *loc. cit.*, 1904, 1197.

(usually kauri gum and rosin), and mixing with it cork flour and various pigments and fillers. The linoleum composition thus obtained is finally rolled on to canvas. A good elastic cement is composed of about 8½ cwt. of oxidised oil, 1 cwt. rosin, and 3 cwt. kauri gum; sometimes copal is added. Each manufacturer, however, uses his own formula, and this is carefully kept as a trade secret. The kauri is pulverised, but the rosin can be used in lumps since it acts as a flux. The mixing operation is carried out in a steam-jacketed vessel provided with stirrers. Samples are withdrawn from time to time and tested. It is of the greatest importance that no overheating takes place. When thoroughly mixed, the "cement" is run into pans, and in summer is sometimes artificially cooled, since large masses of this (as well as the oxidised oil) have been known to heat and spontaneously inflame. The cement is cut into small pieces, mixed with rather more than its weight of ground cork, passed through steam-heated mixing rolls, more thoroughly amalgamated in a mixing drum (various colouring matters being here added according to the colour desired for the finished linoleum) and then passed into a "German"—an apparatus resembling a large sausage machine, but very strongly made. At first steam heating is necessary, but once the machine is working the heat generated by friction keeps the mass soft, and in summer it is even necessary to circulate cold water in the jacket instead of steam. From the "German" the linoleum issues as lumps or pellets, and is passed through mixing rolls, in which it is converted into sheets, and finally is rolled upon jute canvas by means of steam-heated rolls. The canvas back is protected by a varnish ("backing") spread upon it by means of a special machine; the main ingredients of the backing are oxidised oil and varnish, or varnish bottoms mixed with ochres or oxides; the material is fluid when hot, but solidifies on cooling. Finally the linoleum is "seasoned" in rooms at 23.5° C., best in horizontal racks.

Linoleums may be grouped into (1) Plain and Printed; (2) Inlaid; (3) Cork Carpets.

The **Plain Linoleums** consist essentially of cork, pigment, and cement rolled on canvas; they are printed with oil colours so as to produce designs ("**printed linoleums**"). The oil paints, however, in time wear off, and efforts were made to produce coloured patterns running right through the thickness of the coating composition, thus introducing "**inlaid linoleums.**" This requires special machines of extreme ingenuity. Differently coloured linoleum compositions are granulated and moulded into the required shapes, and placed upon the canvas in such a way as to produce the required design; an alternative method is to roll the differently coloured compositions into sheets, and cut from these sheets various forms and stamp them upon the canvas. The patterns thus built up are immediately welded together by heat and pressure, and afterwards seasoned. Details of these special processes will be found in the patent literature. All inlaids contain a large proportion of wood flour in addition to cork dust.

Granite Linoleums are of this class. The "granite" effect is produced by mixing together granules of differently coloured linoleum compositions before pressing the material on to the canvas. In these inlaid linoleums the proportion of cement is generally rather more than that of cork and wood flour, so as to ensure a thorough welding of the various linoleum compositions forming the design.

In **Cork Carpets** the cork grains are larger, and wood dust is never employed, while the quantity of pigment is usually smaller than in the plain and inlaid varieties. Both kinds of cement are used.

Oil-cloth consists simply of fabrics coated with linseed oil, whiting, and pigment, and are printed in oil colours in the usual way.

The colours used in linoleum and oil-cloth manufacture are—

Red.—Red oxides, or, in the case of bright inlaid colours, permanent lakes.
Blue.—"Ultra" blue.
Green.—Chrome green and Brunswick green.

White.—White lead, lithophone.
Yellow.—Chromes.
Black.—Vegetable black.

The authors' best thanks are due to Mr A. H. Dewar, F.I.C., manufacturing manager of the Linoleum Manufacturing Co., Ltd., who gave us much information regarding the modern methods used in manufacturing linoleum.

Statistics.—The amount of **oil-cloth** and **linoleum** imported into the United Kingdom is shown in the following table:—

	Quantities.		Values.	
	1913.	1916.	1913.	1916.
Oil-cloth:—	Sq. Yds.	Sq. Yds.	£	£
For floor coverings	1,333,136	82,211	86,653	5,395
For furniture coverings	524,969	444,561	29,680	11,699
For all other purposes	40,284	18,940	769	533
Total of oil-cloth	1,898.389	545,712	117,102	17,627

	Quantities.		Values.	
	1913.	1916.	1913.	1916.
Oil-cloth:—	Sq. Yds.	Sq. Yds.	£	£
For floor coverings	32,566,000	19,008,200	1.870,118	1,421,723
For furniture coverings	16,898,200	11,685,200	665,950	576,631
For all other purposes	2,454,800	1,364,300	96,280	73,341
Total of oil-cloth	51,919,000	32,057,700	2,632,348	2,071,695

The **United States** in 1910 imported 4,800,000 sq. yds. (value, $1,834,000) of oil-cloth and linoleum; the export of floor oil-cloth reached $128,000 in 1910, the value of other kinds of oil-cloth exported being returned as $353,000.

ANIMAL AND VEGETABLE WAXES (NON-GLYCERIDES)

LITERATURE

See under **Oils, Fats, and Waxes,** Martin's "Industrial Chemistry: Organic," p. 3. Special works dealing with waxes alone are—

L. Sedna.—"Das Wachs und seine technische Verwendung." Vienna, 1902.

T. W. Cowan.—"Wax Craft: All about Beeswax." London, 1908.

The manufacture of ordinary commercial "sealing wax" (which usually does not contain true wax) is dealt with in the following works:—

H. C. Standage.—"Sealing Waxes." London, 1902.

L. E. Andés.—"Siegel- u. Flaschenlacke." (Vienna, 1885.)

W. Ellram.—"Siegel- und Flaschenlackfabrikation." Lodz, 1900.

The waxes are esters formed by the union of fatty acids and alcohols not belonging to the glycerol series. Hence waxes are sharply distinguished from fats in that they contain no glycerol; they have, however, many properties in common with true glycerides (fats); thus they can be saponified with alkalis, the salts of fatty acids and alcohols being obtained:—

$$\underset{\text{The wax ``myricin.''}}{C_{15}H_{31}CO.O.C_{30}H_{61}} + KOH = \underset{\text{Pot. palmitate.}}{C_{15}H_{31}COOK} + \underset{\text{Myricyl alcohol.}}{C_{30}H_{61}OH}$$

The saponification is much more difficult to carry out in the case of waxes than in the case of fats. Wool wax, for instance, must be boiled with alcoholic potash for at least twenty hours; moreover, the higher alcohols, being insoluble in water, occur in the "unsaponifiable" residue. This allows us to readily distinguish fats from waxes; for whereas most fats yield 95 per cent. of fatty acids, the liquid waxes yield only 60-66 per cent., the remaining 40-34 per cent. being made up of monovalent alcohols, among which we may mention:—

Ethane series, $C_nH_{2n+1}.OH$.	Cetyl alcohol	$C_{16}H_{33}.OH$.		Lanolin alcohol	$C_{12}H_{23}OH$.
	Octodecyl alcohol	$C_{18}H_{37}.OH$.	Aromatic alcohols	Cholesterol	$C_{27}H_{45}OH$.
	Carnaübyl ,,	$C_{24}H_{49}.OH$.		Isocholesterol	$C_{26}H_{43}OH$.
	Ceryl ,,	$C_{26}H_{53}.OH$.		Phytosterol	$C_{26}H_{43}OH$.
	Myricyl ,,	$C_{30}H_{61}.OH$.		Sitosterol	$C_{27}H_{45}OH \times H_2O$.
	Psyllostearyl ,,	$C_{33}H_{67}.OH$.			

Liquid Waxes

Sperm Oil, from the blubber and head cavities of the sperm whale, consists of combinations of unknown alcohols with fatty acids. Cooled to low temperatures the oil deposits **spermaceti** (which see). The oil is a valuable lubricant, especially for rapidly running machines; since it does not become gummy or rancid it can be used for delicate machinery such as watches. It retains its viscosity at high temperatures. Sperm oil is used for lubricating, illuminating, dressing leather, and tempering steel.—Sp. gr. (15° C.), 0.880-0.883; sap. val. 123-133; iod. val. 81-84; Reichert-Meissl val. 0.60; fatty acids, 60-64 per cent.; alcohols, 37-41 per cent.; Maumené test, 45°-51° C. If adulteration with fatty acids has taken place glycerol will be found present. The percentage of glycerol multiplied by 10 will give the percentage of fatty oil.

Doegling or Bottlenose Oil is a fluid very similar to sperm oil, with almost identical constants; it can be distinguished from sperm oil by its taste. It has a lower price than the former oil on account of a slight tendency to "gum."

Solid Animal Waxes

Spermaceti, the white crystalline wax which separates from chilled sperm oil, consists principally of cetin (cetyl palmitate), $C_{16}H_{33}O.CO.C_{15}H_{31}$. The substance is a good candle material.—Sp. gr. 0.90-0.96 (15° C.), 0.80-1.81 (100° C.); sol. pt. and M.P. 44° C.; sap. val. 125-134; iod. val. 3.8; alcohols, 51.4 per cent.; fatty acids, 53 per cent.

Beeswax * is obtained from the honeycomb of bees by melting, straining from impurities, and running into moulds. Sometimes the wax is expressed. It may be bleached by exposure to sunlight, or by an oxidising agent such as nitric acid, chromic acid, or hydrogen peroxide. The ordinary yellow wax smells of honey, the bleached is white, inodorous, and tasteless, consisting mainly of myricyl palmitate, $C_{30}H_{61}O.C_{16}H_{31}O$, and cerotic acid, $C_{26}H_{52}O_2$.—Sp. gr. 0.962-0.975 at 15° C., 0.81-0.83 at 100° C.; sol. pt. 60°; M.P. 63° C.; acid val. 20; sap. val. 90; iod. val. 8-11; refract. index, 43°-45° (butyro-refractometer); fatty acids, 47 per cent.; unsaponifiable matter, 55 per cent.; Reichert-Meissl val. 0.3-0.5.

Insect Wax, Chinese Wax, is obtained from an insect, *Coccus ceriferus*, Fabr., or *Coccus pela*, Westwood, which deposits the wax on certain trees. A hard, yellowish-white solid consisting mainly of ceryl cerotate, $C_{26}H_{51}O.CO.C_{25}H_{51}$. This body is used as a furniture and leather polish, for sizing paper and cotton goods, and as a candle material.—Sp. gr. 0.92-97 at 15°, 0.81 at 100° C.; M.P. 81°-83° C.; sap. val. 80-93; iod. val. 1.4; fatty acids, 51 per cent.; alcohols, 49 per cent.

Wool Wax, Wool Grease, is the natural grease encrusting sheep's wool fibre. Before spinning, this grease is removed, sometimes by extracting with volatile solvents, but more usually by washing with soap and sodium carbonate solutions, with which the oil forms an emulsion; on adding sulphuric acid to this the grease separates, as described on p. 15.*

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* A complete account of beeswax, its manufacture and properties, is given by T. W. Cowan, "Wax Craft: All about Beeswax." London, 1908. See also W. F. Reid, *Journ. Soc. Arts* (1903), 522.

The crude grease thus obtained is purified by various patented processes, and brought into the market under the name "**lanolin**." Owing to the ease with which wool wax is absorbed by the skin it forms the basis of many valuable ointments and cosmetics. The chemical composition of wool wax is not exactly known; besides glycerides it contains stearic and palmitic ethers of cholesterol and isocholesterol, as well as the potassium salts of several fatty acids.—Sp. gr. 0.943 (17° C.), 0.90 at 100° C.; sol. pt. 30°; M.P. 36°-42° C.; refract. index (60° C.), 1.465; sap. val. 80-100; iod. val. 20-29; fatty acids, 60 per cent.; alcohols, 43-50 per cent. Mixed fatty acids melt at 41° C.; iod. val. 17; mol. wt. 327. Mixed alcohols, M.P. 33° C.; iod. val. 26-36; acetyl val. 144; mol. wt. 239.

Pure Lanolin is perfectly neutral, does not become rancid, and is very difficult to saponify; its capacity for absorbing water is most remarkable, taking up when kneaded 110 per cent. to form a cream; it similarly takes up glycerin. The skin absorbs it in an extraordinary way, and thus it serves as an excellent basis for introducing effective remedies through the skin; for instance, a lanolin corrosive sublime ointment containing but $\frac{1}{1000}$ per cent. of corrosive sublimate produces a metallic taste upon the tongue within a few minutes of application to any part of the body! Lanolin consequently forms an excellent basis—either hydrated or combined with glycerin—for ointments, pomatums, and cosmetics. It is also employed for superfatting toilet soaps.

Distilled Grease

Yorkshire grease from wool and soap suds is often too dirty and odoriferous to be used for anything except cart grease and rough lubricating materials for rollers, etc. To obtain a better product it is often distilled in cast-iron stills holding about 4 tons of grease, first for ten to sixteen hours over a free fire (to remove water), and then for twenty to twenty-four hours with superheated steam.

"**Spirit Oil**" (*sometimes*, not *always*) comes over first. Pale yellow oil, darkens on keeping, boils over at 150°-320° C. Used in making black varnish.

First Distilled Grease is the second product coming over. It is often allowed to crystallise, and is then pressed for liquid **oleic acid** and solid "**stearine**" (M.P. 48°-57° C.). It is sometimes redistilled ("**second distilled grease**").

The next product to distil is the "**green oils,**" sometimes used for coarse lubricating greases; more often mixed with another batch of material and redistilled.

Pitch remains behind in the still. It is used as a lubricant for the necks of hot rollers.

Wright gives the following numbers for the distillation of 100 parts Yorkshire grease:—Pitch, 14 per cent.; green oil, 15.5 per cent.; first distilled grease, 45.5 per cent.; spirit oil, 4 per cent.; water and loss, 21 per cent. Lewkowitsch finds in distilled grease 55 per cent. free fatty acids; 7 per cent. combined fatty acids; 39 per cent. unsaponifiable matters.

Solid Vegetable Waxes

Carnaüba Wax is exuded by the leaves of the Brazilian wax palm, *Corypta cerifera*, and consists principally of myricyl cerotate. Used in candle manufacture, polishing pastes (wax varnishes), and in making phonograph cylinders.—M.P. 84° C.; acid val. 4-8; sap. val. 79-95; iod. val. 13. True acetyl val. 55; sp. gr. (15° C.), 0.99-1.0, 0.84 at 100°.

Other vegetable waxes are flax wax, gondang wax, pisum wax, opium wax, palm wax, ocuba wax, cotton-seed wax.

The authors desire to thank Mr W. H. Stephens, A.R.C.S., for reading through the above MS. and for several valuable suggestions and corrections.

* *Journ. Chem. Ind.* (1909), 38, 14.

Summary.—The following tables, taken from A. C. Wright's "Analysis of Oils," summarise the chief chemical and physical properties of the better known oils:—

THE CHEMICAL PROPERTIES OF

	Acid Value.*	Saponification Value.	Hehner Value.
Drying oils—			
Linseed oil	1-8	187-196	94.8
Hempseed oil	1	190-195	...
Wood oil	0.7-10.7	(155-) 190-197	96.0-96.6
Candle-nut oil	...	184-192.6	95.5
Walnut oil	10	192-197	95.4
Poppy-seed oil	4-11	189-198	95.0
Niger-seed oil	5-12	189-192	94.1
Semi-drying oils—			
Sunflower-seed oil	0.2-6	190-193	...
Maize oil	2.2-20	187-190	88.2-93.6
Pumpkin-seed oil	3.5-19	188-195	96.2
Sesamé oil	0.2-8	188-192	95.6-95.8
Cotton-seed oil	0.4-2.2	190.4-197	94.2
Rapeseed oil	1.4-4.0	(169.4-) 173-178 (-181)	94.5-96.3
Black mustard oil	5.7-7.4	173-175	96.0
White mustard oil	5.4	170-171	95.8
Non-drying oils and solid fats—			
Earthnut oil	0.3-33	185.6-196	95.6
Almond oil	10	188-195	96.6
Croton oil	...	210.3-215.6	...
Grapeseed oil	16	178-179	...
Castor oil	0.4-0.8	173-183	...
Olive-kernel oil	2.0-3.5	182.3-188	...
Olive oil	0.6-5.0 (-25)	185-195	0.6
Ben oil	...	...	...
Neat's foot oil	0-0.7	194-197.4	95.3-95.5
Lard	...	195.3-196.6	95.8-96.15
Lard oil	0.4	193	97.4
Mahwa butter (*Bassia latifolia*)	4.8-70.8	187-194	94.7, 95.0
Mowrah-seed oil (*Bassia longifolia*)	...	188.4	...
Palm oil	...	196-202	...
Bone fat	...	172-194	86-94
Tallow (beef)	...	193-198	95.6
Tallow (mutton)	...	195	95.5
Tallow oil	...	197	...
Cocoa (cacao) butter	1.1-4.5	191.8-194.5 (-200)	...
Vegetable tallow	...	198.5-203.6	...
Butter fat	0.2-0.6	221-235	86.0-88.8
Palm-kernel oil	...	246-250	..
Japan wax	11-32	(206-212-) 217-222 (-237.5)	90.6
Myrtle wax	3	205.7-211.5	...
Cocoa-nut oil	10.0-35.2	255-263	82.3
Marine animal oils—			
Menhaden oil	0.2	189-192	...
Sardine oil	2.2-21.7	189.8-193.8	94.5-97.1
Cod-liver oil	0.3-31.9	(171-) 175-188	96.5
Seal oil	0.8-43.1	(178-) 189-193	95.4-96.0
Whale oil	0.3-51.4	184-200 (-224)	...
Porpoise oil	0.8	203.4-218.8	...
Dolphin oil	...	197-290	66.3-93
Liquid waxes—			
Sperm oil	0.4	(117-) 125-133 (-147)	...
Arctic sperm (bottlenose) oil	...	123-133	...
Solid waxes—			
Spermaceti	0.1-5	(108) 122.7-136	...
Beeswax	17.5-21	87.5-99	...
Carnaüba wax	4-8	79-95	...
Wool wax	0.6-1.8	83-102.4	...

NOTES (see also the notes appended to the Table of Physical Properties, p. 39).

* The acid values frequently vary greatly; in most cases the higher value given is not to be regarded as a superior limit

† The *total* volatile (soluble) acids may be calculated from the difference between the apparent and true acetyl values determined by Lewkowitsch's method, given in the next column. This difference, multiplied by $\frac{5}{5.6}$, gives (very nearly) the number of c.c. of decinormal potash required to neutralise the volatile acids contained in 1 g. of the fat.

Reichert-Meissl Value.†	Acetyl Value (Lewkowitsch's Method).		Iodine Value.‡	Insoluble Fatty Acids.	
	Apparent.	True.		Saponification Value.	Iodine Value.‡
0 (?)	12.5	11.7	(160-) 170-202	182-199	170-180 (?)
...	...	...	(140-) 155-166	...	141 (?)
...	...	...	150-170	(168)-189	(144-) 150-160
...	...	9.8	(136-140) 163.7	...	142.7-144
0	...	...	143-148	...	...
0	...	..	(120-) 128-137	...	139
0.1-0.6	...	...	126.6-134	...	...
...	...	...	118-132 (-136)	201.5	124-134
4.2-9.9	...	...	(113-) 118-128.6	200.0	121-126.4
...	...	...	113-130.7	...	...
0.35	...	...	104.8-110.4	195-199	109-112
...	7.7	7.6	(97.5-) 102.5-110	201-208	102.4-115
0.0-0.8	...	...	(94-) 98-105 (-110)	174-182	98-105
0	...	...	98.8-106 (-110.5)	...	110
0	...	...	92-96.7	...	96
0	...	...	(82-) 92-105	198	96-103.4
0	...	...	93-102	...	...
12-14	38.6-40.8	...	101-104.7	201	111.2-111.8
0.46	...	...	94-96.2	187	98-99
...	...	146.9	82.6-87	182-193	86.6-94
...	...	...	81.8-87.8	...	...
...	...	...	78-85 (-88)	196-200	86-90
...	...	...	80-84	...	...
...	...	...	67-72.9	200.6-201.2	(63.6-69.5) 74.5-75.8
...	...	...	55-63 (-68.8)	...	59.0-63.5
0	...	...	73-77.3	...	...
0.4-0.9 (1.23)	...	...	(29.9?) 53.4-67.8	206.0	(31.6?)
...	...	...	50.1	...	...
0.5	...	...	50-53.5	205-213	53
...	...	...	46-56 (-62)	201-206	55-57
0.5	6.6	4.6	} average, 41-46 {	196-207	41
...	...	...		...	37.8
...	...	...	71.0-75.7	...	54.6-57
0.2-0.8 (-1.6)	2.8	2.0	32-37.0 (-41)	198	39.1
...	...	...	28-38	202-209.5	30.3-39.5
(11.2-) 24-33 (-41)	...	...	29-37	212.5-217	28-31
5	...	...	10-17	258-265	(3.6-) 12-13.6
(4.7-6 per cent. of soluble acids)	...	...	8.3-12.8	211-216	10.6
...	...	...	10.7	230	...
6.6-8.5	...	...	8.2-9.6	...	8.4-9.3
2.4	...	...	(148-) 175.6-183.1	...	...
...	...	...	134.1-191.7	...	...
0.2	4.75	1.15	(123-) 138.8-177	204	165-170
...	...	...	(91-94-) 125-146	...	...
Reichert value, 3.7-12.5	...	...	(81-) 106-131	...	130-132
22-24	...	...	126.9	...	...
Reichert value, 5.6-66	...	...	33-99	...	...
Reichert value, 1.3	7.1	5.4	78.7-84	...	...
...	6.7	5.4	80.4-82.1	...	...
...	4.6	2.6	4	...	...
...	17.4	15.2	8.8-10.7	...	...
...	57.5	55.2	13.5	...	...
...	32.6	23.3	(10-) 20-21 (-28)	...	...

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‡ Iodine value. Low results were obtained in the older determinations owing to the use of an insufficient excess of the reagent. Low results in the case of the drying oils may also be due to the sample having undergone oxidation. Thus the lower figures given in the table represent values which may not now be expected.

THE PHYSICAL PROPERTIES OF THE OILS, FATS, AND WAXES

	Specific Gravity.	Melting Point.	Solidifying Point.	Refractive Index	The Insoluble Fatty Acids.		
					Specific Gravity.	Melting Point.	Solidifying Point.
Drying oils—		° C.	° C.			° C.	° C.
Linseed	$\frac{15.5}{15.5}$ 0.930-0.937 $\frac{99}{15}$ 0.8809	−16 to −20	16, −27	15° C., 1.481 60° C., 1.4674	$\frac{15.5}{15.5}$ 0.923, $\frac{100}{100}$ 0.8925	17-24	13-17
Hemp-seed oil	$\frac{15}{15}$ 0.925-0.933	...	−27.5	...	...	17-19	16
Wood oil	$\frac{15.5}{15.5}$ 0.934-0.943	...	Below −17(?)	...	...	30-49	17-34
Candle-nut oil	$\frac{15.5}{15.5}$ 0.9256	...	...	15° C., 1.4756-1.4759	...	20-21	13
Walnut oil	$\frac{15.5}{15.5}$ 0.921-0.926	...	...	40° C., 1.4689-1.4710	...	16-20	14-3
Poppy-seed oil	$\frac{15.5}{15.5}$ 0.923-0.9268 (0.937)	..	−18	40° C., 1.4680	...	20-21	16-19
Niger-seed oil	$\frac{15.5}{15.5}$ 0.9248-0.9270	...	Below −9	40° C., 1.4678	...	...	...
Semi-drying oils—							
Sunflower-seed oil	$\frac{15}{15}$ 0.924-0.926	...	...	...	...	22-24	17-19.8
Maize oil	$\frac{15.5}{15.5}$ 0.924-0.928	...	−36	15° C., 1.4765-1.4767 60° C., 1.4605	100° C., 0.8529	17-22.4	...
Pumpkin-seed oil	$\frac{15}{15}$ 0.917-0.925	...	−15	25° C., 1.4723-1.4738	...	26.5-28.5	...
Sesamé oil	$\frac{15}{15}$ 0.921-0.926	..	...	15° C., 1.4746 60° C., 1.4580	...	24.2-31	18-28
Cotton-seed oil	$\frac{15.5}{15.5}$ 0.920-0.928 $\left(\frac{15}{15}\ 0.930\right)$	...	...	15° C., 1.475 60° C., 1.4586	$\frac{100}{100}$ 0.8816	35-40	32-38
Rape-seed oil	$\frac{15.5}{15.5}$ 0.912-0.917	...	−1 to −10	15° C., 1.4745 60° C., 1.4584	$\frac{100}{100}$ 0.8758	17-21	12-16.5
Black mustard oil	$\frac{15.5}{15.5}$ 0.915-0.919	...	−17.5	40° C., 1.4655	...	16-17	15
White mustard oil	$\frac{15.5}{15.5}$ 0.912-0.915	...	−8 to −16	40° C., 1.4649	...	15-16	...

Non-drying oils and solid fats—							
Earth-nut oil	$\frac{15.5}{15.5}$ 0.916-0.9256	...	−3 to −7	15° C., 1.4731 60° C., 1.4564	$\frac{100}{100}$ 0.8475-0.864	27-32	22-30
Almond oil	$\frac{15.5}{15.5}$ 0.917-0.9195	...	−10 to −21	25° C., 1.468-1.467 60° C., 1.4555	...	14	5-14
Croton oil	15° C., 0.940-0.960; 100° C., 0.8874	...	−16	27° C., 1.4768	...	...	16.4-19
Grape-seed oil	15° C., 0.920-0.596	..	−10 to −17	...	...	23-25	18-20
Castor oil	$\frac{15.5}{15.5}$ 0.960-0.967	..	−10 to −18	15° C., 1.4803 60° C., 1.4647	...	13	3
Olive-kernel oil	$\frac{15}{15}$ 0.918-0.920	...	...	1.4682-1.4688	...	...	...
Olive oil	($\frac{15}{15}$ 0.914) $\frac{15.5}{15.5}$ 0.917-0.920 $\frac{100}{100}$ 0.862-0.864	..	...	15° C., 1.4718 60° C., 1.4546	$\frac{60}{15}$ 0.878 $\frac{100}{100}$ 0.8749	22-26	21-24
Ben oil	$\frac{15}{15}$ 0.9120	.	..	...	...	...	...
Neat's foot oil	$\frac{15}{15}$ 0.914-0.919	..	...	15° C., 1.473 60° C., 1.4559	$\frac{100}{100}$ 0.8742-0.8800	28-30	16-26.5
Lard	$\frac{15}{15}$ 0.931-0.938 $\frac{60}{15.5}$ 0.886 $\frac{100}{15}$ 0.860-0.862	40-45	27-30	40° C., 1.458-1.460 60° C., 1.452	...	35-45	37-39
Lard oil	$\frac{15.5}{15.5}$ 0.917 100°, 0.8626	..	...	...	0.885	35	31
Mahwa butter (*Bassia latifolia*)	$\frac{100}{100}$ 0.8943-0.8975	23.0-31.0	19-22	40° C., 1.4605-1.4609	...	45	40
Mowrah seed oil (*Bassia longifolia*)	100° C., 0.8854	35.5-42	25-36	...	...	54.5-55.5	52.5
Palm oil	$\frac{60}{15.5}$ 0.8837 $\frac{100}{100}$ 0.858	...	...	60° C., 1.451	$\frac{100}{100}$ 0.870	47-50	40-45
Bone fat	$\frac{15.5}{15.5}$ 0.914-0.916 $\frac{60}{15.5}$ 0.894	21-22	...	60° C., 1.451	...	30-42	28-32

THE PHYSICAL PROPERTIES OF THE OILS, FATS, AND WAXES (*continued*)

	Specific Gravity.	Melting Point.	Solidifying Point.	Refractive Index.	The Insoluble Fatty Acids		
					Specific Gravity.	Melting Point.	Solidifying Point.
Non-drying oils and solid fats (*cont.*)		° C.	° C.			° C.	° C.
Tallow (beef)	$\frac{60}{15.5}$ 0.901, $\frac{100}{100}$ 0.860	42-48	...	40° C., 1.4987 60° C., 1.442	...	45-47	42.5-45
Tallow (mutton)	$\frac{60}{15.5}$ 0.907	47-51	...	60° C., 1.4531	...	45-50	43-46
Tallow oil	$\frac{100}{100}$ 0.794	...	...	...	...	...	35-37.5
Cocoa (cacao) butter	$\frac{100}{100}$ 0.903-0.904	23.5-33	...	40° C., 1.448-1.458 60° C., 1.450-1.458	...	45-51	47.2-49.2
Vegetable tallow	...	37-46	24-31	...	...	40-57	34-48
Butter fat	$\frac{40}{15.5}$ 0.904-0.9102 $\frac{100}{15}$ 0.865-0.870 $\frac{100}{100}$ 0.909-0.914	29-34.6	19-20	25° C., 1.459-1.462 60° C., 1.445-1.450	$\frac{20}{20}$ 0.9106-0.9242	38-43	...
Palm-kernel oil	$\frac{60}{15.5}$ 0.896, $\frac{99}{15}$ 0.873	23-28	...	40° C., 1.450 60° C., 1.443	...	21-28	...
Japan wax	$\frac{60}{15.5}$ 0.902-0.907 $\frac{98}{15.5}$ 0.875	42-45	...	60° C., 1.450	..	56-57	53-56.5
Myrtle wax	$\frac{98}{15.5}$ 0.875	40-44	39.5-43	...	$\frac{99}{15.5}$ 0.837	47.5	46.0
Cocoa-nut oil	$\frac{60}{15.5}$ 0.897- $\frac{99}{15.5}$ 0.874	...	...	40° C., 1.445-1.450 60° C., 1.442	...	24-27	19-23
Marine animal oils—							
Menhaden oil	$\frac{15.5}{15.5}$ 0.932-0.935	...	-4	...	...	...	...
Sardine oil	$\frac{15}{15}$ 0.925-0.928 $\left(\frac{15}{15}\ 0.916\text{-}0.933\right)$	20-22	...	15° C., 1.479	...	30-31	...
Cod-liver oil	$\frac{15.5}{15.5}$ 0.922-0.935	...	...	15° C., 1.482 60° C., 1.462-1.466	$\frac{60}{60}$ 0.882	21-25	...

Seal oil	$\frac{15}{15}$ 0.924-0.927	—	...	15° C., 1.478 60° C., 1.4619	...	...	...
Whale oil	$\frac{15}{15}$ 0.920-0.927	—	...	15° C., 1.476 60° C., 1.460	...	...	...
Porpoise oil	$\frac{15}{15}$ 0.926-0.927	...	−16	...	...	...	...
Dolphin oil	$\frac{15}{15}$ 0.918	...	...	...	...	...	...
Liquid waxes—							
Sperm oil	$\frac{15.5}{15.5}$ 0.875-0.886	...	...	15° C., 1.467 60° C., 1.4508	$\frac{15}{15}$ 0.899	13.3	...
Arctic sperm (bottlenose) oil	$\frac{15.5}{15.5}$ 0.880	...	...	...	...	10.3-10.8	...
Solid waxes—							
Spermaceti	$\frac{98}{15.5}$ 0.808-0.816	43-49	42-45	...	...	...	...
Beeswax	$\frac{15}{15}$ 0.961-0.970	62-65	...	...	...	...	...
Carnauba wax	$\frac{15}{15}$ 0.99-1.0	83-86	...	...	...	...	...
Wool wax	$\frac{15}{15}$ 0.973, $\frac{60}{15.5}$ 0.885	36-43	...	60° C., 1.465	...	41.8	40

Notes

It has not been thought necessary to quote the authorities for the figures in this table.

Figures in brackets represent abnormal results, possibly due to the examination of a genuine oil of unusual character, or of a sample which has undergone modification through keeping.

CHAPTER XI

Analysis of Fatty Oils

CHAPTER XI.

ANALYSIS OF FATTY OILS

(See also Appendix II., p. 199).

Methods of Examination.—Only in exceptional cases (such as sesamé oil and cotton-seed oil, which contain characteristic compounds) is it possible to directly identify a given fatty oil by means of a reagent, and it is therefore necessary to apply physical and chemical tests, which will locate the oil in successively narrowing groups, and finally to apply similar tests of identity.

The methods employed include a determination of the so called "constants" or values of the sample, such as the specific gravity, solidification and melting points, optical properties, amount of iodine absorbed (iodine value), amount of alkali required for saponification (saponification value), amount of volatile and insoluble fatty acids present in the oil (Reichert and Hehner values), etc.

The difficulty of the task is often increased by the fact that oils and fats of the same kind show considerable variations in their constants—so much so that an oil—*e.g.*, olive oil—may contain a considerable proportion of an adulterant such as maize oil, and still show values falling within the higher limits recorded for the pure natural oil. This will be seen more clearly in the following details concerning the "values."

Specific Gravity.—This is usually determined at a temperature of 15.5° C. in the case of oils and at 100° C. in the case of solid fats, water at 15.5° C. being taken as unity. *Tables of Specific Gravities* are given on pp. 142-147. The sp. gr. of **butter fat** is best taken at 35° C. The sp. gr. of oils and fats often increases with age, and sometimes varies with the method of refining the oil.

The following table, based on a system first proposed by Allen, illustrates the assistance given by the specific gravity in the classification of oil.

OILS.

Sp. gr. 0.913-0.920 (15.5° C.).	Sp. gr. 0.920-0.925 (15° C.).	Sp. gr. 0.925-0.935	Sp. gr. 0.935-0.960 (15.5° C.).
Almond oil.	Cotton-seed oil.	Linseed Oil.	Tung oil.
Colza ,,	Maize ,,	Whale ,,	Castor ,,
Arachis ,,	Sesamé ,,	...	Croton ,,
Olive ,,	Cod-liver Oil.		...

FATS AND WAXES.

Sp. gr. 0.800-0.855 (100° C.).	Sp. gr. .855-0.[illegible]3 (100° C.).	Sp. gr. 0.863-0.867 (100° C.).
Spermaceti.	Palm oil.	Coco-nut oil.
Beeswax.	Cacao butter.	Japan wax.
...	Tallow.	Butter fat.
..	Lard.	...

Method.—A hydrometer is employed if the quantity of oil is large. When the amount of oil available for testing is small we use a specific gravity bottle or a Sprengel or Nicol pycnometer. The latter gives results of great accuracy. The pycnometer or specific gravity bottle is calibrated by filling up to the mark with distilled water at 15° C., and weighing it. Then the bottle is emptied and dried, and filled with the oil at 15° C., and the weight of oil ascertained.

The specific gravity is the weight of a given volume of oil at 15° C., as compared with the same volume of water at 15° C. The symbol used to denote this is $d. \frac{15^\circ}{15^\circ}$.

When the fat is solid it is heated to the temperature of the boiling water bath (about 99° C.), and the bottle filled up to the mark with the fat at this temperature, the whole being kept at this temperature by immersion in boiling water. The weight of oil or fat thus found is then compared with the weight of the same volume of water at 15° C., and the specific gravity thus obtained is represented by $d. \frac{99^\circ}{15^\circ}$.

Free Fatty Acids and Rancidity.—Gradual decomposition of the glycerides into their components, glycerol and free fatty acids, takes place when a fat is exposed to the action of light and air, with the result that the oil becomes "rancid." Hence the quantity of free fatty acids present in an oil is a test of its freshness or rancidity, according as the quantity of free fatty acids is high or low. Old and rancid fats have very high acid values. The permissible limit for free acidity depends on the nature of the fat or oil. Edible tallows should not have more than 3 per cent., lard more than 0.5 per cent., and coco-nut oil 2 per cent. (See *Table*, p. 196, for *permissible amounts of free fatty acids in oils*. See *Table*, p. 54, for "Acid Values" of certain oils.)

Free acidity is determined by weighing out 2-18 g. of fat (according to the degree of acidity), and dissolving at gentle heat in 25 c.c. of industrial alcohol (previously neutralised by N/10 caustic soda, using phenolphthalein), and then titrating with N/2 or N/10 aqueous or alcoholic caustic potash or sodium hydroxide, using phenolphthalein as indicator, and shaking well after each addition of alkali, until a slight permanent pink colour is produced (see p. 201).

The results are usually expressed in terms of oleic acid (1 c.c. N/10 alkali equals 0.0282 g. oleic acid), 100 parts of fat being stated to contain the calculated amount of oleic acid; but in the case of coco-nut oil, palm-kernel oil, etc., the acidity is calculated as *lauric acid* (see p. 201). (1 c.c. N/10 alkali equals 0·02 g. lauric acid.)

Example.—2.000 g. of fat were taken, and required 5 c.c. of N/10 caustic soda for neutralisation.

$$\frac{5\cdot0 \times 0\cdot0282 \times 100}{2\cdot000} = 7\cdot05 \text{ per cent. free fatty acids expressed as oleic acid.}$$

$$\frac{5\cdot0 \times 0\cdot02 \times 100}{2\cdot000} = 5.0 \text{ per cent. ,, ,, ,, lauric acid.}$$

The free acidity is sometimes expressed as "**Acid Value,**" which is the number of milligrammes of KOH necessary to neutralise the free acid in 1 g. of fat or oil. In the foregoing example we have:—

$$\frac{5\cdot0 \times 5\cdot61}{2\cdot000} = 14\cdot02 \text{ Acid Value (see also p. 201).}$$

Refractive Index.—Oils frequently show pronounced differences in their refractive index—so much so that this value when determined by means of a refractometer at a definite temperature may afford decisive proof of adulteration. Thus in the case of butter fat Wollny obtained readings varying from 1.4560-1.4620, while margarine gave readings of 1.4650-1.4700, and mixtures of butter and margarine readings of 1.4620-1.4690.

The different forms of apparatus employed are described fully in the catalogues of firms supplying chemical apparatus, and so will not be described here.

We may mention, however, that the refractive index may be directly determined by an Abbé total reflection refractometer, or an Amagat and Jean oleo-refractometer, as described in the *Analyst*, 1890, 87. More usually, however, a special instrument, termed a "butyro-refractometer," in which the readings are given in degrees on a scale, is widely employed for this purpose, and is particularly useful as a sorting test. As is evident, however, from the examples quoted above, a mixture of butter with a small percentage of margarine may give refractometer readings falling within the limits of those of genuine butter. (See *Tables*, pp. 142 to 147.)

The great advantage of this test is the ease and rapidity with which a number of samples can be examined. The Abbé and Zeiss instruments require only 5 or 6 drops of oil to carry out a test.

The refractive index for oils is usually determined at 60° C. Butter is usually determined at 40° C.

Melting and Solidification Points.—The temperatures at which fats or oils melt or solidify also afford means of identifying different samples. For instance, almond oil does not solidify until chilled to − 20° C., whereas olive oil solidifies at about 2°-4° C. These differences largely depend upon the nature of the fatty acids in the glycerides. Thus olive oil contains a large proportion of the glycerides of solid fatty acids, whilst in almond oil such glycerides are only present in traces, the oil consisting chiefly of glycerides of liquid fatty acids. (See *Tables*, pp. 142-147.)

The "**Titre**" or melting points of the separated fatty acids may also afford valuable information. The following are a few solidifying points of fatty acids obtained from various oils and fats (the numbers represent centigrade degrees):—

Beef tallow, 38-46.
Mutton tallow, 41-48.
Lard, 34-42.
Horse fat, 33·7.
Neat's-foot oil, 26.5.
Palm oil, 36-45.
Coco-nut oil, 20-25.
Palm-nut oil, 20-25.
Japan wax, 59.
Vegetable tallow, 45 53.
Linseed oil, 13-17.

Tung oil, 37.
Hemp oil, 14-16.
Poppy-seed, 16.5.
Cotton-seed, 32 36.
Rape, 12-18.
Olive, 17-26.
Arachis, 23-29.
Cod-liver, 18-24.
Whale, 24.
Japanese sardine, 28

The melting point of fats is determined by drawing out a piece of thin glass tubing into a capillary tube. The fat is melted in a small glass beaker, and the end of the capillary tube dipped into the melted fat. This is sucked up by capillary action into the tube. The tube is withdrawn and allowed to cool, when the fat solidifies. Next the tube is tied to the stem of a thermometer, so that the bulb and the fat in capillary tube are close together. The whole is immersed in a beaker of cold water placed on a sand bath or on gauze, and the beaker is gradually heated by a Bunsen burner.

The fat suddenly becomes transparent and liquid at its melting point, and rises in the tube. The temperature at which this occurs is read off on the thermometer, and gives the melting point of the fat.

The Titre or Solidifying Points of the Fatty Acids, introduced by Palicer, is the test now most usually adopted. In this the solidifying point of the fatty acids separated from a fat or oil is determined, and not that of the oil itself.

Thirty grammes of the fat are melted in a shallow porcelain basin, and 30 c.c. of a 25 per cent. solution of sodium hydroxide are added, together with 50 c.c. of redistilled industrial alcohol. The mass is stirred on the water bath and evaporated until a pasty mass of soap is formed. Then another 50 c.c. of industrial alcohol are added, which redissolves the soap, and the whole is evaporated to drying, with stirring, on the water bath.

The solid soap thus obtained is dissolved in distilled water, and slight excess of dilute sulphuric acid added to liberate the fatty acids, and the whole is warmed until the separated fatty acids melt to a clear oily liquid on the surface. The water underneath the oil is now siphoned off, and more distilled water added to wash out mineral acid, and again siphoned off, this treatment being continued until the washings are no longer acid to litmus paper. The melted fatty acids are poured on to a dry filter paper, which is inserted in a funnel resting on a beaker, and the latter is placed on the water bath, where it is left until the clear fatty acids have filtered through.

Next 10-15 g. of these dry fatty acids are placed in a wide test tube, 6 in. long and 1 in. in diameter. This is inserted through a cork into a flask or wide-mouthed bottle to protect the tube from too sudden variations of temperature. The tube is closed by means of a loosely fitting perforated cork through which passes a short range thermometer (0° 60° C.) accurately graduated in $\frac{1}{10}$th of a degree centigrade. The bulb of the thermometer is immersed in the fatty acids as near the centre as possible.

The temperature is now raised a few degrees above the melting point of the fatty acids, and they are allowed to cool-down without stirring. When the fatty acids just begin to solidify at the bottom of the tube, the thermometer is stirred round slowly. The temperature gradually falls until a minimum point is reached, and then the temperature begins to rise owing to the heat given out by the fatty acids in crystallising. The maximum temperature attained by the fatty acids during this increase is called the "titre" of the sample.

The commercial valuation of tallows and the uniformity of the hardness of the fats used in making margarine (a very important factor) are usually determined by this test.

Saponification Value.—The oil is boiled with a measured excess of alkali in suitable solution, and the amount (expressed in milligrammes of potassium hydroxide) required to effect complete decomposition of 1 g. of the fat into soap and glycerol or other alcohol is termed the saponification value. (See p. 202.)

As the fatty acids possess different molecular weights, the proportion of alkali required to neutralise them will also vary, and the oils containing them will have different saponification values. (See *Tables*, pp. 142-147.)

By way of example, the following saponification values may be quoted :—

Castor oil, 176-183.
Cod-liver oil, 182-187.
Cotton-seed oil, 192-193.
Olive oil, 190-195.
Linseed oil, 190-195.
Almond oil, 190-192.
Lard, 195-196.
Butter fat, 225-230.

Coco-nut oil, 255-260.
Beeswax, 90.
Paraffin wax, 0.
Wool wax, 102.
Insect wax, 90.
Spermaceti, 123-134.
Sperm oils, 123-136.

Hence, if a sample of lard showed a saponification value of, say, 200, the presence of coco-nut oil would be suggested and further tests for that fat would be applied.

NOTE.—(1) Waxes, both liquid and solid, are characterised by such low saponification values that they are easily distinguished by this means from oils.

(2) The majority of oils and fats have saponification values about 193. Higher or lower values than this may suggest the presence of special oils.

(3) Mineral oils have a zero saponification value, and consequently their presence lowers the saponification value of a fatty oil.

Practical Details.—The saponification value is determined by weighing out into a 200 c.c. conical flask about 2 g. of the fat or oil, then adding 25 c.c. of neutral industrial alcohol and 25 c.c. of approximately N/2 alcoholic solution of potassium hydroxide. The same quantities of methylated spirit and alcoholic potassium hydroxide are placed in another flask in order to carry out a blank test. The two flasks are fitted with reflux condensers and placed on the water bath, and boiled until the fat is completely saponified (30-60 minutes), which occurs when all globules of oil have disappeared. A little phenolphthalein is now added to each flask and N/2 sulphuric acid run in from a burette until the pink colour is just discharged. (See also p. 202.)

The difference in the amount of acid required by the two flasks gives the amount of potassium hydroxide to saponify the weight of oil or fat taken.

Example.—2.30 g. of fat require 9.8 c.c. of N/2 sulphuric acid in order to neutralise unabsorbed alkali. In the blank test 25 c.c. of the approximately N/2 alcoholic potassium hydroxide solution required 25.8 c.c. of N/2 sulphuric acid to neutralise it. Hence $25.8 - 9.8 = 16.0$ c.c. of N/2 potassium hydroxide solution is required to saponify 2.30 g. of fat. Hence 1 g. of fat requires $\frac{16.0}{2.30} = 6.96$ c.c. N/2 KOH $= \frac{56 \times 6.96 \times 1000}{1000 \times 2} = 194.9$ mg. of KOH. This is the "saponification value."

The Ester or Ether Value is the number of milligrammes of KOH required for the saponification of the neutral esters or glycerides in 1 g. of fat. It is obviously the difference between the "saponification value" and the "acid value" (p. 152).

Note.—A convenient method of working is to use 2 g. of fat or oil and determine the "acid value" as described on p. 152, and then add 25 c.c. of approximately N/2 alcoholic potassium hydroxide solution and determine the saponification value as just described. (See also p. 202.)

Unsaponifiable Matter.—In order to determine this 5 g. of the fat or oil are boiled for one hour with 50 c.c. of approximately N/2 alcoholic potash solution, using a reflux condenser and agitating the flask frequently. The solution is then evaporated to dryness on the water bath, and the resultant soap dissolved in 200 c.c. hot water, and the solution is allowed to cool, transferred to a separating funnel, shaken with 50 c.c. of ether, and allowed to stand. The ethereal layer is removed to another separator, and the process repeated twice with more ether. The three ethereal extracts are now washed with water to remove any dissolved soap, separated; transferred to a weighed flask, and the ether distilled off upon the water bath. The residue is dried in the oven at 100° C. until constant, and represents the "unsaponifiable matter." It is calculated to per cent. on the oil. (See also p. 202.)

Practical difficulties are often met with in carrying out this determination, owing to the fact that a distinct separation of ether and aqueous soap solution sometimes does not occur, as an intermediate layer of emulsion persists even after prolonged standing. The addition of alcohol (when petroleum ether is used), glycerine, water, more ether or potash solution may be tried in order to overcome this effect. Also gentle rotatory agitation is often efficient.

Nature of the Unsaponifiable Matter.—This may consist of cholesterol (a constituent of many animal fats), phytosterol (found in vegetable fats), cetyl and ceryl alcohols (found in spermaceti and Chinese wax), or hydrocarbons, which are occasionally added as an adulterant of animal or vegetable fats.

In order to detect **mineral oils, paraffin wax**, and other unsaponifiable matters in fats, we proceed thus: Saponify with alcoholic potash, evaporate to dryness on the water bath, extract the unsaponifiable matter with petroleum spirit or ether, evaporate the solvent, and the residue represents the amount of unsaponifiable matter. The saponification is effected thus: Weigh out 10 g. fat into a porcelain basin, add 50 c.c. of 8 per cent. alcoholic potash solution, boil on water bath until soap begins to froth, then add 15 c.c. alcohol and boil until the soap is dissolved. Stir into the mass 5 g. sod. bicarbonate and 50-60 g. recently ignited pure white sand; dry twenty minutes in water oven, transfer to a Soxhlet apparatus, extract with petroleum spirit (B.P. below 80° C.), distil off petroleum spirit and weigh residue. **Waxes** require prolonged boiling for complete saponification, but are more easily saponified if boiled with a freshly-made solution of sodium (5 g.) in absolute alcohol (100 c.c.). The **Soxhlet apparatus** used for extraction is shown in the figure. The substance to be extracted is placed in the tube *a*, which is closed at *f*. In *b* petroleum spirit is placed and heated to boiling point. The vapour rises through *c* into the condenser *d*, and, descending in the form of drops, gradually fills *a* with liquid to the level of the bend in the tube *e*; when this happens, the liquid siphons over into the flask *b*, bearing with it the extracted matter. Then the process begins anew, a continual stream of solvent flowing through *a* until all the extractible matter is removed from the substance. The fluid in *b* is then distilled, and the extracted matter remaining behind is dried at 100° and weighed.

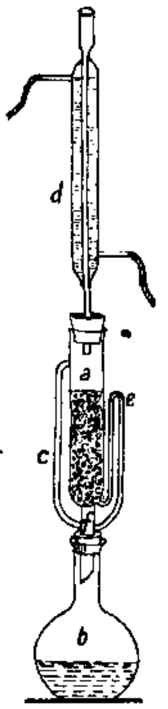

FIG. 68.—Soxhlet Fat Extraction Apparatus.

To Distinguish Between Animal and Vegetable Oils and Fats

Animal Oils and fats contain the alcohol **cholesterol**, $C_{27}H_{46}O$. **Vegetable fats** contain a similar alcohol called **phytosterol**, $C_{27}H_{46}O$. This fact allows us to distinguish between animal and vegetable fats. If the fat contains *both* cholesterol and phytosterol it is a mixture of animal and vegetable fats. To test for **cholesterol** and **phytosterol**, dissolve a small portion of the unsaponifiable matter in acetic anhydride. Add one drop of solution to one drop of 50 per cent. sulphuric acid placed on a white tile. A characteristic blood-red to violet colour is produced. If cholesterol or phytosterol are found present proceed as follows: Saponify a considerable quantity of fat by alcoholic potash; the cholesterol or phytosterol remains in the unsaponifiable matter. If the body is a wax, saponify with sodium dissolved in absolute alcohol.

1. Dissolve the unsaponifiable matter in ether, filter if necessary, evaporate off the ether, redissolve in absolute alcohol, and allow to crystallise on a watch glass; examine crystals under the microscope. Crystals of cholesterol form laminæ and have a different shape from those of phytosterol (needle-shaped tufts).

2. Heat crystals obtained in 1 with 2-3 c.c. of acetic anhydride in a small dish covered with a watch glass; evaporate off the acetic anhydride on the water bath and crystallise twice from alcohol. Take melting point in the usual way..

Cholesteryl acetate melts at 114°-115°; **Phytosteryl acetate** melts at 125°-137° C. Hence they are easily distinguished.

If both cholesteryl and phytosteryl acetates are present fractionally crystallise the mixture several times from alcohol, and thus separate the crystals into high melting and low melting portions, and examine these separately.

According to Bömer (*Zeit. Untersuch. Nahr. Genussm.*, 1898, 81) an acetate melting at 117°-118° C. corresponds to an addition of 1-2 per cent. of vegetable oil; and at 123°-125° C. an addition of 3-4 per cent. of vegetable oil.

Additional Tests for Cholesterol.—1. A few drops of the unsaponifiable matter are dissolved in 2-3 c.c. of glacial acetic acid. Add a little benzoyl peroxide and boil solution. Next add four drops of strong sulphuric acid; when a violet-blue or green colour is produced, the violet-blue being due to oxycholesterol ester, and the green to oxycholesterol (Lifschutz, *Ber. Deut. Chem. Ges.*, 1908, 252-255).

2. Add to a small quantity of the unsaponifiable matter a mixture of five parts of concentrated sulphuric acid, and three parts of formaldehyde solution, when cholesterol will be turned a blackish-brown colour (Golodetz, *Chem. Zeit.*, 1908, 160).

3. Dissolve a little of the unsaponifiable matter in trichloracetic acid, and add one drop of a 30 per cent. formaldehyde solution, when an intense blue colour is produced if cholesterol is present (Golodetz, *loc. cit.*).

Moisture in Oil.—Five to twenty grammes of fat are weighed out into a previously weighed porcelain dish, and stirred with a thermometer while being heated at about 100° C. by a gas flame until bubbling and crackling has ceased. The loss of weight represents the water. If spurting occurs a little alcohol added will carry off the water quietly. For a much better method, see p. 200.

Davis (*Journ. Amer. Chem. Soc.*, 23, 487) prevents spurting by adding the oil to a previously dried and weighed filter paper contained in a stoppered weighing bottle. The whole is then dried at 100° C. in the oven until constant in weight. Obviously this method is inapplicable to oils and fats which oxidise on heating. In this case use the method described on p. 200.

Dregs, Fibre, Adipose Tissue, Dirt, etc.—From 10-15 g. of the fat are dissolved in petroleum ether, with stirring, and passed through a weighed filter paper (previously dried and weighed at 100° C.). The residue retained by the filter paper is washed with petroleum ether until free from fat, and is dried in the water oven at 100° C. and weighed. (See also p. 201.)

If much residue is left, ignite and determine nature of ash.

Tate estimates impurities by weighing 5 g. of fat into a separating funnel, dissolving in ether, and allowing to stand six hours in order to separate the water. The water is run off, the tube of separator dried, and the ethereal solution filtered through a dried weighed filter paper into a weighed flask. The filter is washed with ether and dried at 100° C. The ether in flask is recovered by distillation, and the flask dried until its weight is constant.

The amount of fat in flask gives actual fat in sample taken: the loss in weight represents water and other impurities. The latter can be estimated by weighing the filter paper.

Starch is detected by the blue colour it gives with iodine. A microscopical examination gives the kind of starch.

By heating with acids, starch can be inverted to glucose, and the latter estimated by Fehling's solution.

Iodine Value.—The liquid fatty acids, which form the principal constituent of the glycerides in fluid oils, are unsaturated compounds, and will combine with bromine or iodine (in suitable form) to form saturated bodies. The percentage of iodine absorbed in this test is termed the iodine value, and is a most valuable means of identifying different groups of oils.

One class of oils, typified by almond and olive oils, consists largely of oleic acid (which absorbs approximately 90 per cent. of iodine). These have iodine values of about 80-95, and are known as **non-drying oils.**

Another group contains oils in which linolic acid (absorbing about 181 per cent. of iodine) is an important constituent. Cotton-seed oil (iodine value, about 108), sesamé oil (iodine value, 110), and maize oil (iodine value, 120) are examples of these oils, which are termed **semi-drying oils.**

A third important group contains the **drying oils,** in which the glyceride of linolenic acid (iodine value, 274) is usually an important constituent. They naturally have high iodine values, *e.g.*, linseed oil, 195; nut oil, 142.

Marine animal oils also have high iodine values, due to the presence of highly unsaturated fatty acids, but they may be distinguished from drying oils by their non-drying properties, and by other tests.

Solid fats have iodine values which are greater in proportion to the amount of unsaturated fatty acids they contain. Lard, for instance, usually has an iodine value of 50-60, so that a high iodine value (*e.g.*, 70) points to the lard having been stiffened with beef fat, and then rendered sufficiently fluid again by the addition of a vegetable oil, such as maize or cotton-seed oils.

Certain kinds of American lard, however, normally have high iodine value (up to 66), and it is therefore necessary to confirm the presence of a vegetable oil in lard by other tests (see p. 155).

IODINE VALUES OF COMMON OILS, FATS, AND WAXES (see p. 143).

Oleic acid, 90.
Tallow, 35-46.
Butter, 36-48.
Lard, 50-65.
Mutton fat oil, 32-57.
Oleo-margarine, 53-88.
Olive oil, 79-93.
Sesamé oil, 103-112.
Rape oil, 94-108.
Cotton-seed oil, 105.
Castor oil, 83-86.
Arachis oil, 90-103.
Palm oil, 51-57.
Coco-nut oil, 8-9.
Palm-kernel oil, 10-17.
Croton oil, 101-109.
Linseed oil, 179-200.
Tung oil, 149-167.
Sunflower oil, 118-136.
Hemp-seed oil, 140-166.
Poppy-seed oil, 137-143.
Walnut oil, 143-148.
Seal oil, 127-146.
Whale oil, 121-146.
Cod-liver oil, 154-181.
Shark liver, 115.
Menhaden oil, 175-183.
Sardine oil, 161-193.
Porpoise oil, 131.
Sperm oil, 81-84.
Arctic sperm oil, 67-82.
Insect wax, 1.4.
Beeswax, 10.
Spermaceti, 4.
Wool wax, 17.
Carnaüba wax, 13.

NOTES.—(1) Linseed oil has a high iodine value, and adulteration with foreign oils lowers that value.

(2) The addition to walnut or poppy-seed oil of 5-10 per cent. of rape or cotton-seed-oils and 20 per cent. linseed has an influence on the iodine value.

(3) The adulteration of olive oil with only 5 per cent. of a drying oil and 15 per cent. of cotton-seed, sesamé, rape, or arachis oil may be suggested by the iodine value.

(4) Fish oils have very high iodine values, and their presence is thus indicated in oils with low iodine values but not in drying oils.

(5) If I denotes the iodine value of a mixture of two fats whose iodine values are m and n respectively, then **percentage of fat** $m = \frac{100(I - n)}{m - n}$.

Determination of Iodine Values.—Two main methods are used:—

1. **Hübl's Method.**—The reagents required are (1) a solution of 25 g. iodine in 500 c.c. absolute alcohol. (2) A solution of 30 g. mercuric chloride in 500 c.c. absolute alcohol. These two solutions are kept separate, and are only mixed together and allowed to stand twelve to twenty-four hours before use. (3) A freshly prepared 10 per cent. aqueous solution of potassium iodide. (4) An N/10 sodium thiosulphate solution, standardised prior to use against resublimed iodine dissolved in potassium iodide solution.

0·2-0·6 g. of fat is weighed into a tightly fitting stoppered bottle; 10 c.c. chloroform is added, and 25 c.c. of the mixed Hübl solution is run in from a burette. The bottle is then firmly stoppered, and allowed to stand for four hours in a dark place. A blank test is simultaneously carried out by placing the same quantities of chloroform and Hübl solution in a similar bottle, and placing the two bottles side by side.

After standing four hours, 20 c.c. of the freshly prepared 10 per cent. potassium iodide solution and 150 c.c. of water are added to each bottle, and the excess of iodine titrated with the recently standardised N/10 sodium thiosulphate, the bottles being shaken well during each titration, and fresh starch solution being used for determining the final point.

The number of c.c. of thiosulphate required in the blank experiment is deducted from the number of c.c. required by the other bottle, and the difference is a measure of the iodine absorbed by the fat. This figure multiplied by the iodine equivalent of 1 c.c. of the thiosulphate, and by 100, and divided by the weight of fat taken, gives the "iodine number," *i.e.*, the weight of iodine absorbed by 100 g. of fat.

Example.—1 c.c. of the N/10 thiosulphate solution is equivalent to 0·0130 g. iodine.

0·540 g. of fat was taken. The blank experiment required 59·9 c.c. thiosulphate, while the bottle containing the oil required 24·8 c.c. of the thiosulphate.

59·9 − 24·8 = 35·1 c.c., and the iodine absorption of the part is:—

$$\frac{35{\cdot}1 \times 0{\cdot}0130 \times 100}{0{\cdot}540} = 84{\cdot}5$$

2. **Wij's Method** has now to a very large extent displaced Hübl's method, because the iodine is absorbed by the fat in about thirty minutes, against several hours required by Hübl's process. Here the iodine reagent consists of a solution of iodine monochloride dissolved in glacial acetic acid. It can be prepared by weighing out 7·9 g. of iodine trichloride in a stoppered weighing bottle, and 8·7 g. iodine, dissolving these separately in glacial acetic acid, mixing and making up to a litre with glacial acetic acid. More usually, however, 13 g. of iodine are dissolved in 1 litre of glacial acetic acid, and chlorine is passed into the solution until the iodine is converted into the iodine monochloride—a point which may be determined by the gain of weight (13 g. iodine increasing by 3·5 g.), or, after practice, by the change in the colour of the solution.

The rest of the process is carried out exactly as in the Hubl process, but it is usually better to dissolve the fat in carbon tetrachloride instead of in chloroform. Full details of procedure are given in Appendix II., p. 203, which the reader should consult.

Soluble and Insoluble Fatty Acids

Hehner Value.—This test devised by Hehner indicates the percentage of insoluble fatty acids which can be separated from an oil or fat. It is usually about 93-96, but in the case of fats (such as butter, coco-nut oil, and palm oil) which contain a high proportion of volatile and soluble fatty acids it is much lower. Thus butter usually has a Hehner value ranging from 85-88, and coco-nut oil a value of 88-90.

We give a few numbers; for others see *Table*, p. 142:—

100 g.	**cow's butter fat**	contain	86-89	g.	insoluble fatty acids.
,,	tallow	,,	96	,,	,,
,,	lard	,,	96	,,	,,
,,	olive oil	,,	95	,,	,,
,,	poppy seed	,,	95	,,	,,
,,	palm oil	,,	96	,,	,,
,,	palm kernel	,,	91	,,	,,
,,	coco-nut oil	,,	89	,,	,,
,,	dolphin jaw oil	,,	66	,,	,,
,,	porpoise jaw oil	,,	70	,,	,,

Practical Details.—5 g. of the fat are placed in a strong 6-oz. bottle, and 56 c.c. of approximately N/2 alcoholic potassium hydroxide solution are added, while another 50 c.c. are placed in an empty flask.

The bottle is firmly closed by an india-rubber stopper, which is wired on, and is then placed in the water bath and heated for about thirty minutes until saponification is complete (shown by contents of bottle being free from oily globules). During the heating the bottle is occasionally removed, and the contents agitated by shaking well, care being taken not to bring the liquid into contact with the stopper. When saponification is complete, the bottle is removed from water bath and allowed to cool. The contents of bottle are transferred to a 250 or 300 c.c. flask (well rinsing out bottle with boiling water), and this is placed, together with the flask containing only alcoholic potassium hydroxide solution, on the steam bath until all the alcohol has evaporated.

The contents of each flask are now neutralised with N/2 hydrochloric acid, 1 c.c. acid being added in excess, and the exact amount of acid used is noticed.

The flask containing the fat is now nearly filled with boiling water, and placed on the water bath, after inserting a cork fitted with a long upright tube.

As soon as the fatty acids have melted to a clear liquid on the surface of the water, the flask is removed and allowed to cool until the fatty acids solidify. By gently tapping the flask this cake of fatty acids is loosened from the sides, and the liquid poured through a filter into a large flask.

The flask containing the insoluble fatty acids is again filled with hot water, the cork and reflux tube replaced, [illegible] the liquid gently heated to the boiling point. The flask is next thoroughly shaken until [illegible] melted fatty acids are emulsified with the water, after which the fatty acids are allowed to se[illegible]te again on the surface and solidify to a solid cake, which is again loosened by tapping, and [illegible] liquid filtered off as before. This operation is repeated three times (or until the washings co[illegible]d separately do not require more than 0·2 c.c. of N/10 sodium hydroxide for neutralisation). The mixed washings are now made up to 1 litre, and part titrated with N/10 sodium hydrox[illegible], the number of c.c. required being calculated upon the whole liquid.

This amou[illegible]f alkali represents the amount required to neutralise the soluble fatty acids in the water, togethe[illegible]ith the excess of acid added after saponification. The latter is ascertained by titrating the [illegible]ess in the blank experiment, so that the difference between these two titrations gives the alka[illegible]bsorbed by the volatile fatty acids.

The solu[illegible] fatty acids are usually calculated as butyric acid, C_3H_7COOH. 1 c.c. of N/10 sodium hydr[illegible]e represents 0·0088 g. butyric acid. Hence :—

$$\text{\% soluble fatty acid} = \frac{\text{No. c.c. N/10 NaOH} \times 0{\cdot}0088 \times 100}{\text{Weight of fat taken}}.$$

Re.

The ins[illegible]le **fatty acids** are estimated by draining the flask containing the solid cake, melting [illegible], and pouring them on to the wet filter through which the soluble fatty acids have They are then washed on the filter with boiling water, and the funnel filter placed in aker in the water bath until all the fatty acids have filtered through. Flask, filter paper, l are next well washed with ether, the washings added to the filtered fatty acids, and the aporated and the fatty acids dried at 100° C. until constant in weight. From the weight ined is calculated the weight of insoluble fatty acids yielded by 100 g. of fat. This fehner Value."

ichert Value.—This is a measure of the amount of alkali, expressed in decinormal solution, required to neutralise the proportion of volatile soluble acids liberated and distilled under the constant conditions laid down by ert. A modification of the method devised by Meissl is more commonly yed, the value being termed the **Reichert-Meissl** value, and relating to 5 g. ad of 2·5 g. of the fat. The following are a few typical Reichert-Meissl values others see *Table*, p. 143):—

Butter fat, 28 c.c. (24-33).
Beef tallow, 0·5 c.c.
Olive oil, 0·6 c.c.
Sesamé oil, 0·7 c.c.
Rape oil, 1·0 c.c.
Palm oil, 1·0 c.c.
Palm-kernel oil, 5 c.c.

Coco-nut oil, 7-8 c.c.
Maize oil, 0·3-4·4 c.c. (Reichert).
Croton oil, 13 c.c.
Dolphin oil, 11 c.c.
Dolphin jaw oil, 130 c.c.
Porpoise body oil, 46 c.c.
Porpoise jaw oil, 100-139 c.c.

Most of the solid animal body fats have only trifling Reichert-Meissl values, but a butter fats the proportion of volatile fatty acids is high, and correspondingly high lues are obtained in the test.

Thus in the case of cow's butter the value normally ranges from about 24 to out 33. Hence when a sample of butter shows a Reichert value of, say, 20, the ddition of an adulterant is probable. In the case of certain kinds of Dutch cows, however, the butter fats sometimes give a value as low as 17, this being attributed to leaving the herds in the fields too late in the season.

Most vegetable oils and fats have a Reichert-Meissl value of less than 2, but coco-nut oil has a value of 7-8, and palm-kernel oil a value of about 4. A considerable amount of these fats may, therefore, be added to butter without rendering the Reichert value suspiciously low.

Of late several methods of detecting these fats in butter have been based upon a separation of the fatty acids intermediate between the quite insoluble acids and hose readily volatile. Coco-nut oil and palm-kernel oil are particularly rich in hese acids, and therefore show an "extended" Reichert value, which is not given butter.

Determination of the Reichert-Meissl Value (see the *Analyst*, 1900, 309) :—

2·15
mixtu **olloy's Modification.**—Five grammes of the fat are introduced into a 300 c.c. flask, of the
Th hown in Fig. 69 (length of neck 7·8 cm., width of neck 2 c.c.). Two c.c. of a 98 per cent.
this oc soda solution in an equal weight of water—preserved from the action of atmospheric carbon
occurs a

dioxide—and 10 c.c. of 92 per cent. alcohol are added, and the mixture is heated u[illegible] denser connected with a flask by a T-piece, for fifteen minutes in a bath containin[illegible] The alcohol is distilled off by heating the flask on the water bath for about thirty [illegible] the soap is dry. 100 c.c. boiling water, which has been kept boiling for at le[illegible] are added, and the flask heated until the soap is dissolved.

Forty c.c. of normal sulphuric acid and three to four fragments of pumice or broken pipe[illegible] added, and the flask is at once connected with a condenser by means of a glass tube 7 mm. [illegible] 15 cm. from the top of the cork to the bend. At a distance of 5 cm. above the top of the [illegible] bulb 5 cm. in diameter. The flask is supported on a circular piece of asbestos, having a ho[illegible] centre 5 cm. in diameter, and is first heated by a very small flame, to fuse the insoluble fatty [illegible] but the heat must not be sufficient to cause the liquid to boil. The heat is increased; and [illegible] fusion is complete 110 c.c. are distilled off into a graduated flask, the distillation lasting [illegible] thirty minutes (say from twenty-eight to thirty minutes), the distillate is shaken, 110 c.c. filte[illegible] transferred to a beaker, 0·5 c.c. phenolphthalein solution (1 g. in 100 c.c. of alcohol) [illegible] and the filtrate titrated with N/10 soda or baryta solution until pink. A blank experiment is [illegible] out in exactly the same way, using the same reagents but omitting the fat.

The amount of N/10 soda required to neutralise this distillate should not exceed 0·3 c.c. and

The difference between the number of c.c. of alkali required with the fat and in 13 g. determination, multiplied by 1·1, gives the Reichert-Meissl-Wollny value.

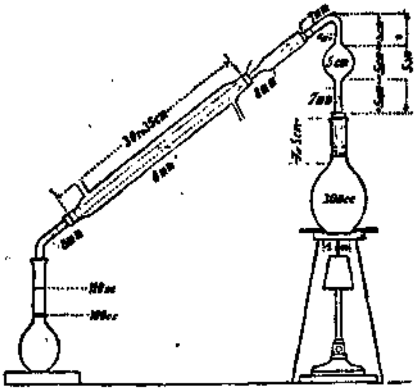

FIG. 69.—Wollny's Apparatus for Determining the Reichert-Meissl Value.

The Polenské Value

This measures the volatile insoluble fatty acids which distil in the determinat of the Reichert-Meissl value.

Five grammes of the filtered fat are placed in a 300 c.c. flask (Fig. 70) with 20 c.c. of glycerine and 2 c.c. of a solution of sodium hydroxide in one part of water, and heated over a free flame.

The soap solution is allowed to cool below 100° C., diluted with 90 c.c. of water, and heated on the water bath at about 50° C. until the soap dissolves. The hot soap solution must be clear and nearly colourless. It is acidified with 50 c.c. of dilute sulphuric acid (25 c.c. conc. sulphuric to 1,000 c.c. water), and a few fragments of pumice, and the flask is connected with a condenser as shown in Fig. 70, and heated. The heat is regulated so that nineteen to twenty minutes suffice for the distillation of 110 c.c. The distillate running into the collecting flask must have a temperature between 20° C. to 23° C.

After 110 c.c. distillate has collected, the flask is replaced by a 20 c.c. graduated cylinder. The flask is then immersed up to the neck in water at 15° C., avoiding shaking in so doing. Any oily drops which separate after five minutes are made to stick to the sides of the flask by tapping th[illegible] neck. The flask is cooled for a further ten minutes in the water, and is then closed by a cork a[illegible] gently inverted several times in order to mix the contents.

100 c.c. of the distillate are filtered through paper 8 cm. in diameter, and the filtrate titrated [illegible]10 alkali, as in the ordinary method of determining the Reichert-Meissl value, and this [illegible]luble volatile fatty acids.

[illegible] insoluble volatile acids on the filter are washed three times with three successive [illegible] water, each of which has been run through the condenser tube; next the liquid [illegible] the flask, and the washings (containing the soluble volatile acids) are thrown

The insoluble volatile acids sticking to the sides of the flask, cylinder, and condenser are now removed by three successive rinsings (15 c.c. each time) with 90 per cent. alcohol (previously neutralised). These alcoholic washings are poured over the filter, each being allowed to drain off before the next is added.

The **alcoholic filtrate** is now titrated with N/10 alkali solution, and this gives the measure of the **insoluble volatile fatty acids.**

The number of c.c. required is the **Polenské Value.**

The main *use* of the **Polenské value** is to determine whether a butter fat contains coco-nut oil.

Coco-nut oil contains more insoluble fatty acids than butter fat, and consequently has a much higher Polenské value, *e.g.*, butter fat having Reichert-Meissl values of 23-30 showed Polenské values of 1·5-3·0, whereas coco-nut oil with Reichert-Meissl values of 6·8-7·7 possessed Polenské values of 16·8-17·8.

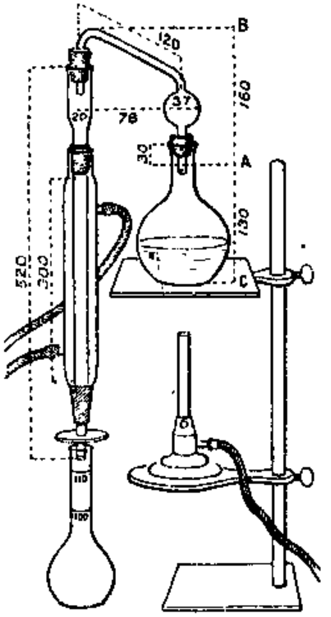

FIG. 70.—Apparatus for Determining the Polenské Value.

Revis and Bolton state that if a butter fat gives a Polenské value exceeding by 0·5 c.c. the corresponding Reichert-Meissl value indicated in the following table, it is certain that the butter fat is adulterated with coco-nut oil or palm-kernel oil :—

TABLE

Reichert-Meissl value - - -	32	31	30	29	28	27	26	25	24	23
Corresponding Polenské value - -	3·5	3·2	3·0	2·9	2·7	2·4	2·0	1·8	1·7	1·6

Valenta's Acetic Acid Test.—Principally used for ascertaining the purity of butter fat, 2·15 g. fat and 3 c.c. glacial acetic acid are warmed to 40° C. If the butter fat is pure the mixture becomes clear.

The liquid is now allowed to cool slowly until it just becomes cloudy. In the case of pure butter this occurs between 30° and 40° C. In the case of some sorts of margarine, the clear solution only occurs at 97° C. to 94° C.

Maumené Test.—Weigh 50 g. of oil into a 200 c.c. tall beaker packed with cotton wool into litre beaker; *run in slowly (take sixty seconds) from a* burette 10 c.c. of concentrated sulphuric acid, stirring continually with a thermometer; the highest temperature attained is the required value.

Olive oil, 42° C.
Almond oil, 52°-54° C.
Rape oil, 57°-60° C.
Arachis oil, 45°-75° C.
Sesamé oil, 68° C.
Cotton-seed, 75°-90° C.
Poppy-seed, 88° C.
Walnut, 101° C.
Hemp-seed, 98° C.
Linseed, 103°-145° C.
Castor, 47° C.

Tallow oil, 41°-44° C.
Neat's-foot, 48° C.
Cod-liver, 102°-103° C.
Skate-liver, 102° C.
Menhaden, 126° C.
Seal, 93° C.
Whale, 92° C.
Porpoise (body), 51° C.
Sperm, 51° C.
Arctic sperm, 41°-47° C.

Drying oils have a high Maumené value; so also have fish oils. Non-drying oils have a low value.

Elaïdin Test.—Useful for detecting drying oils mixed with non-drying, and *vice versa*. Measure 50 c.c. of oil into a wide-mouthed stoppered bottle of 100 c.c. capacity; add 2 c.c. of cold, freshly-made mercury nitrate (prepared by dissolving 13 g. mercury in 12 c.c. concentrated nitric acid, keeping cold in cold water to retain nitrous fumes), shake well; place in air oven at 25° C. for twenty-four hours, agitating from time to time; simultaneously perform a comparison experiment with a standard sample of oil, and compare results. Note length of time of solidification and consistency of mass after twenty-four hours.

Drying Oils (linseed, hemp-seed, walnut, poppy, etc.) remain *fluid*.

Semi-drying Oils (rape, neat's-foot, sperm, cotton-seed, etc.) yield after twenty-four hours a thick mass of treacle-like consistency.

Non-drying Oils (olive, sperm, tallow, etc.) turn into a solid mass.

The following examples show the use of these constants in analytical work:—

1. A sample of oil sold as olive oil had the following characteristics: Sp. gr. 0·924; acid value, 4; saponification value, 190; iodine value, 105; refractometer reading, 67; melting point of fatty acids, 24° C.

The iodine value at once indicated that this was not pure olive oil, and the other values agreed with those of pure sesamé oil. This was confirmed by a special colour reaction for that oil, and by the fact that it slowly dried on exposure in a thin film to the air.

2. A solid fat sold as lard gave the following results: Iodine value, 72; and Reichert-Meissl value, 2·5. The high iodine value suggested the presence of a vegetable oil, and this was found by special colour reactions to be cotton-seed oil. The Reichert-Meissl value indicated the presence of coco-nut oil, and this was confirmed by other tests.

Differentiation of Fish Oils from Drying Oils.—Oils such as cod-liver oil (and marine animal oil, whale, etc.) may be distinguished from linseed and other drying oils by drying tests, and by the fact that on treatment with bromine they yield an insoluble white compound, which turns black when heated.

The corresponding compound from linseed oil treated in the same way melts to form a colourless liquid. The following list gives the percentage yield of insoluble bromides from certain typical oils:—*

Linseed, 24-38.
Tung oil, *nil*.
Candle-nut oil, 8.
Walnut oil, 1·4-1·9.
Poppy-seed oil, *nil*.
Maize oil, *nil*.
Cotton-seed oil, *nil*.
Brazil-nut oil, *nil*.
Olive oil, *nil*.

Almond oil, *nil*.
Fish oil (deodorised), 50.
Cod-liver oil, 30-43.
Japan fish oil 2.
Shark-liver, 20.
Seal oil, 28.
Whale oil, 15-26.
Sperm oil, 2·4-3·7.

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[*] This test was originated by C. A. Mitchell. Lewkowitsch and others invariably describe these insoluble bromides as "hexabromides." They are the bromides of mixed glycerides and certainly not hexabromides.

CHAPTER XII

Manufacture and Analysis of Butter

CHAPTER XII

MANUFACTURE AND ANALYSIS OF BUTTER

The Manufacture of Butter

BUTTER can be made from fresh or sour cream or from whole milk. Generally the cream is allowed to sour or ripen before being churned. This gives a larger yield of butter and the flavour is better. The ripening of cream is accelerated by keeping it at a fairly warm temperature, 60°-70° F., and using a starter. The starter may be a pure culture of some lactic acid bacteria, or a little sour milk or buttermilk. First pasteurising the cream and then employing a pure starter is the best means of obtaining cream of the required ripeness, and butter made under these conditions is much more uniform in character.

The composition of butter according to Storch is :—

	From Fresh Cream.	From Ripened Cream.
Water	13·03 per cent.	13·78 per cent.
Fat	83·75 ,,	82·97 ,,
Protein	0·64 ,,	0·84 ,,
Milk sugar	0·35 ,,	0·39 ,,
Mineral substances	0·14 ,,	0·16 ,,
Salt	2·09 ,,	1·86 ,,

It is thus seen that 83-84 per cent. of butter is fat, and the rest is water with small quantities of protein, milk sugar, mineral matter, and 1-2 per cent. of salt which has been added in the making.

The percentage of water in butter is liable to considerable variations, and may reach as much as 20 per cent. In this country 16 per cent. is regarded as the maximum limit.

In the churning of cream the globules lose their spherical shape and collect in larger particles, which usually have a granular form. The evenness of grain of the butter after churning is of importance, and attention is paid by the maker to this point. Well ripened cream, churned at the proper temperature and not too long, gives butter of a good grain.

When the butter has been got into this granular state, it must be thoroughly washed to remove the buttermilk, which otherwise would cause the butter to rapidly become rancid. The temperature at which this is done is also of importance.

When the butter has been washed as free from buttermilk as possible, it is salted, and for this purpose a pure salt is required. It should be free from magnesium salts, otherwise it tends to become moist and then set in hard lumps, which prevents an even distribution of salt through the butter.

The manufacture of butter on a large scale is carried out in precisely the same manner as on a small scale, except that the churns and workers are run by machinery.

In America, in Germany, and to a less extent in Ireland, machines which combine a churn and a butter worker have been introduced into butter factories, so that it is now possible to work, wash, and salt the butter in the same vessel as that in which it was churned. The best known of these machines are the Astra and the Simplex. Attempts have been made to combine a separator with the churn and butter worker, and in Sweden at the present time several of these machines are in use.

Pure butter varies considerably in appearance, colour, taste, and smell, according to the breed of the cow, the food, the time of the year, and method of making. As has already been mentioned in speaking of milk, the fat which is present in the cream in an undercooled state passes into the solid condition on being made into butter. Butter is characterised by the relatively high percentage of glycerides of the lower fatty acids. Other fats contain a much smaller quantity of these glycerides, so that a determination of the percentage of lower fatty acids serves as one of the best methods for the detection of adulteration with some animal fat such as margarine. When the fatty acids are isolated from butter fat it is found that the following are present:—

Butyric acid	$C_4H_8O_2$	(volatile)	Myristic acid	$C_{14}H_{28}O_2$	(non-volatile)
Caproic ,,	$C_6H_{12}O_2$	,,	Palmitic ,,	$C_{16}H_{32}O_2$	,,
Caprylic ,,	$C_8H_{16}O_2$	,,	Stearic ,,	$C_{18}H_{36}O_2$	,,
Capric ,,	$C_{10}H_{20}O_2$	,,	Arachidic ,,	$C_{20}H_{40}O_2$	,,
Lauric ,,	$C_{12}H_{24}O_2$	(non-volatile)	Oleic ,,	$C_{18}H_{34}O_2$	,,

The proportions in which these acids are present in normal butter are subject to variation, but it is generally found that the glycerides of the first four make up 8-9 per cent. of the total. Almost certainly the glycerides are mixed, that is to say, the glycerine group is combined with different acid radicals, so that butter can hardly be regarded as a mixture of simple triglycerides. There is difficulty in proving this, but Partheil and Velsen, who made an artificial butter from the triglycerides of fatty acids, in the proportion in which they are present in butter, found that it had a higher solidifying point than natural butter.

The specific gravity of pure butter fat at 100° is from 0·865-0·868, the melting point varies from 28°-34·7° C., the solidifying point from 19°-23° C.

Butter fat is insoluble in water, soluble in alcohol, and very soluble in ether, chloroform, benzine, petroleum ether, etc.

The usual **analysis of butter** is confined to the estimation of the water, the fat, and the salt, and the determination in the pure butter fat of the amounts of soluble fatty acids, insoluble fatty acids, the refractive index, and the iodine value.

Water.—Samples having been taken from the bulk by means of a sampler like a cheese borer, they are put into a wide-mouthed stoppered bottle, which is then placed in warm water (40° C.). The fat, when melted, is shaken vigorously, and about 5 g. are poured into a porcelain dish containing pieces of pumice stone. The dish is then dried at 100° until the weight is constant, or very nearly so. It is not advisable to dry the butter for longer than three hours, for the continued heating tends to change its composition.

A rapid method for the estimation of water is to simply heat the butter in a dish, stirring all the time with a glass rod. When the butter ceases to froth and the casein has a brown colour, all the water has been driven off, and the dish is allowed to cool and is again weighed.

Fat.—The dried fat and pumice stone from the previous experiment are transferred to an extraction cartridge, which is then placed in a Soxhlet extractor. The dish from which the butter and pumice have been scraped is washed out well with ether, which is poured over the cartridge, and the extraction is proceeded with in the ordinary way. A layer of extracted cotton wool should be placed on the top of the cartridge to prevent fine particles of pumice stone from being carried over.

The Röse-Gottlieb method is also very useful for the estimation of the fat. Weigh out 2 g. of butter on fat-free paper, and place it in the Gottlieb tube, add warm water to make up to 10 c.c. (as for milk), then 1 c.c. of ammonia and 10 c.c. of 95 per cent. alcohol. Shake the whole well, cool the tube, and shake out with ether and petroleum ether, as in the analysis of milk.

Salt.—This can be estimated by dissolving a known weight of butter in ether, to which a little water has been added. The salt dissolves in the water, the fat in the ether, and the two can be separated with a separating funnel. The aqueous solution is then titrated with decinormal silver nitrate, neutral potassium chromate solution being used as the indicator.

Another method is to ignite the butter carefully in a small platinum dish, extract the sodium chloride from the ash with water, and titrate as above.

An examination of the butter fat is necessary to determine whether adulteration with some other fat has taken place. A pure sample of the fat is obtained by melting the butter at a temperature of 40°-50° C., and filtering it through a dry filter.

The refractive index is usually determined with a Wollny-Zeiss butter refractometer. Full details of how to use this instrument are supplied by the makers (Carl Zeiss, Jena), and it will therefore suffice to note that at 25° C. natural butter fat has a refractive index of 49·5-54·0 divisions. At 40° C. the number of divisions on the same instrument is from 40·55-44·4, and fat in exceptional cases 47.

Margarine fat has a higher refractive index—58·6-66·4 divisions at 25° C., and 48-52 divisions at 40° C., so that it is possible to detect adulteration with margarine if considerable quantities have been used. The refractive index will hardly serve to detect small quantities, for the figures obtained for genuine butter vary too much. Another substance used in considerable quantities for adulteration of butter is coco-nut fat, and this has a refractive index of 33·5-35·5 at 40° C.

There are several well-known chemical tests for the purity of butter fat, of which the following deserve notice :—

1. **The Reichert-Meissl Value** (p. 159).—Pure butter fat may have a Reichert-Meissl value as low as 20 or as high as 34, but it is seldom that genuine butter falls below 24. Margarine in which a very small quantity of these lower fatty acids is found has a Reichert-Meissl value of 1 or 2, not more as a rule.

2. **The Hehner Value** (p. 158) for genuine butter fat can vary from 85·5-91 ; the average value is 87.5. In margarine the value is higher.

3. **The Koettstorfer or Saponification Value** (p. 153) is very high for butter, lying between 220.5 and 332 for butter fat. This serves to detect adulteration with many fats whose saponification value is much less.

4. **The Iodine Value** (p. 156).—The iodine value of pure butter fat lies between 25·7 and 49, and it is particularly useful in detecting adulteration with coco-nut fat.

The above are the chief tests employed in the chemical examination of butter fat. As margarine is the most usual adulterant of butter, its peculiarities as compared with butter fat have been noticed. See **Margarine Manufacture**, p. 173 ; also p. 175.

Colouring of Butter

Butter is nowadays usually coloured, except perhaps during a few of the summer months. The public demand is for a bright yellow butter, so that if the article fails to have the desired colour the sale is prejudiced. The materials used in the colouring of butter are generally harmless in their effect upon the consumer, and the practice is not prohibited by health authorities.

In this country, **Annatto**, which is got from the fruits of the *Bixa orellana* tree, is usually employed. The colouring matter after extraction is dissolved in some vegetable oil. In this condition the annatto is easily incorporated with the butter, and an even yellow colour is obtained. Too much annatto gives a reddish unnatural colour to the butter, and this should be avoided.

Saffron, curcuma, extract of marigolds, juice of carrots, are all used as butter colours. Latterly, some of the well-known yellow aniline dyes have been used for colouring butter, and whilst there is no evidence that they are injurious to health in small quantities, it would doubtless be preferable to use one of the vegetable substances previously mentioned.

Tests for Colouring Matter in Butter and Margarine

"Lactochrome," the natural colouring matter of butter, is insoluble in alcohol, ether, glacial acetic acid, and similar solvents. So that if a coloured extract is obtained on extracting the fat with these solvents then undoubtedly an artificial colouring matter has been added.

1. **Leeds' Scheme of Analysis** (A. R. Leeds, *The Analyst*, 1887, 150).—100 g. of fat are mixed with 300 c.c. of light petroleum spirit (sp. gr. 0·638) and well shaken. The ethereal extract is separated by means of a separating funnel, and washed with 100 c.c. of water in small quantities at a time. The ethereal extract is allowed to stand fifteen to twenty hours (best surrounded by ice) and is decanted from any separated fatty matter. The extract is next shaken with 50 c.c. of N/10 potassium hydroxide solution, the alkali extract is separated, rendered faintly acid with

dilute hydrochloric acid, and the precipitated colouring matter, together with a trace of free fatty acid which is always dissolved out by the alkali, filtered off and subjected to the tests given in the following table:—

LEEDS' COLOUR TESTS

Colouring Matter.	Concentrated Sulphuric Acid.	Concentrated Nitric Acid.	Sulphuric Acid and Nitric Acid.	Concentrated Hydrochloric Acid.
Annatto.	Indigo blue, turning to violet.	Blue, becomes colourless on standing.	Same.	No change, or possibly slight dirty yellow and brown.
Annatto and decolorised butter.	Blue, becomes green, and slowly changes to violet.	Blue, becomes green and then colourless.	Decolorised.	No change, or possibly slight dirty yellow and brown.
Turmeric.	Pure violet.	Violet.	Violet.	Violet, on evaporating off HCl turns to original colour.
Turmeric and decolorised butter.	Violet to purple.	Violet to reddish violet.	Same.	Fine violet.
Saffron.	Violet to cobalt blue, changing to reddish brown.	Light blue, changing to light reddish brown.	Same.	Yellow, changes to dirty yellow.
Saffron and decolorised butter.	Dark blue, rapidly changing to reddish brown.	Blue, turns green and then brown.	Blue, rapidly becoming purple.	Yellow, becomes dirty yellow.
Carrot.	Umber brown.	Decolorised.	Decolorised, with red fumes and odour of burnt sugar.	No change.
Carrot and decolorised butter.	Reddish brown to purple, similar to turmeric.	Yellow and decolorised.	Same.	Slightly brown.
Marigold.	Permanent dark olive green.	Blue, instantly changing to dirty yellow.	Green.	Green to yellowish green.
Safflower.	Light brown.	Partially decolorised.	Decolorised.	No change.
Analine yellow.	Yellow.	Yellow.	Yellow.	Yellow.
Martius yellow.	Pale yellow.	Yellow reddish precipitate, magenta at margin.	Yellow.	Yellow precipitate.
Victoria yellow.	Partially decolorised.	Same.	Same.	Same colour, returns on neutralising with ammonia.

2. **Cornelison's Scheme of Analysis** (*Journ. Amer. Chem. Soc.*, 1908, 1478).—10 g. of the melted fat are thoroughly agitated with 10-20 g. of glacial acetic acid at 35° C. The mixture is allowed to separate and the acid layer drawn off. The colour of the acid extract is noted, and it is then treated as in the following table. One part colouring matter to 100,000 parts of butter or margarine give the indicated results.

CORNELISON'S COLOUR TESTS

Dye.	Colour of Acid Extract.	Concentrated Nitric Acid.	Concentrated Sulphuric Acid.	Sulphuric Acid and Ether to Clear Solution.
(Pure natural butter.)	Colourless.	Colourless.	Faint pink on standing.	Colourless.
Sudan I. (pure).	Decided pink.	Strong pink.	Strong clear pink.	Pink.
Butter yellow (impure).	Very faint pink.	Faint pink.	Faint pink.	Faint colour.
Cerasine orange G. (Casella).	Strong greenish yellow.	Acid yellow, oil-globule, salmon-pink.	Same.	Brownish yellow.
Yellow O.B. (Heller and Merz).	Decided bright yellow.	Acid faint pink, oil-globule, salmon-pink.	Same.	Pink.
Annatto.	Dull yellow.	Little change.	Faint pink on standing.	Very faint yellow.
Curcumine.	Intense greenish yellow.	Dull ochre yellow.	Strong pink.	Yellow.
Carrot.	Very faint greenish yellow.	Faint yellow.	Faint pink on standing.	Very faint yellow.
"Alderney butter colour" (Heller and Merz).	Brownish yellow.	Strong pink.	Strong pink.	...
Ranson's butter colour ("Vegetable").	Yellow.	Almost decolorised.	As with HNO_3.	...
"Dandelion brand" butter colour ("Vegetable").	Yellow.	Almost decolorised.	As with HNO_3.	...

Preservatives.—Certain preservatives are added to increase the keeping properties of butter. Boracic acid and its salts are the usual preservatives.

Boron Compounds.—(*a*) **Detection.**—Mix butter with excess of water in mortar, pour off water, acidify water with a drop of hydrochloric acid, moisten a piece of turmeric paper with the solution, and dry in steam oven. Boron compounds cause paper to develop reddish pink tint, turned deep blue when moistened with weak alkali.

(*b*) **Estimation.**—(1) Richmond-Harrison-Thomson process: 25 gr. fat are placed in a 100 c.c. stoppered cylinder, and after the moisture present has been determined, enough water is added to bring the total water present up to such a quantity that 1 c.c. corresponds to 1 gr. of butter. 10-15 c.c. of chloroform are run in, the flask heated, shaken, and liquid allowed to separate. An aliquot part of the liquid is now removed by a pipette, evaporated dry, ignited, and residue extracted with hot water. The extract is made neutral to methyl orange, boiled to expel carbon dioxide, half its volume of glycerine added, and the mixture titrated with N/10 sodium hydroxide solution until pink to phenolphthalein. Each c.c. N/10 sodium hydroxide corresponds to 0·0062 gr. of boracic acid.

Tests for Benzoic Acid, Salicylic Acid, Beta Naphthol, and Fluorides

Extract the melted butter with a dilute solution of sodium bicarbonate, and examine this extract for the various preservatives.

E.g., **Benzoic** and **salicylic** acid are detected by exactly neutralising solution with dilute hydrochloric acid, and adding ferric chloride.

Benzoic acid or benzoate gives a buff-coloured precipitate.

Salicylic acid gives an intense violet coloration.

Text-books on practical organic chemistry should be consulted for other tests for these organic substances.

Fluorides in absence of boric acid may be detected by evaporating a small quantity of the alkaline extract to dryness in a platinum crucible, igniting residue, moistening with concentrated sulphuric acid, and etching a glass plate covered with paraffin wax, which is placed over the mouth of the crucible, after having some marks scratched on it.

If boric acid is present, the fluoride may volatilise away as boron fluoride. In this case add lime water until liquid is alkaline, thereby fixing the boric acid as calcium borate.

Evaporate dry, and extract residue with dilute acetic acid. This dissolves out the calcium borate. The insoluble matter is then treated with concentrated sulphuric acid as above.

CHAPTER XIII

The Manufacture and Analysis of Margarine

11 FEB. 1927

CHAPTER XIII

THE MANUFACTURE AND ANALYSIS OF MARGARINE

LITERATURE

Most of the facts in the accompanying article were supplied privately by firms interested in the manufacture of margarine. Much of the published literature is very poor, and often describes methods in vogue over twenty years ago and now abandoned.

G. HEFTER.—"Technologie der Fette u. Öle." Vol. III. Berlin, 1910. Gives the best account.

LEWKOWITSCH.—"Oils, Fats, and Waxes." Vol. III. (1901 edition).

Dr K. WINDISCH.—"Margarinekase." Berlin, 1898.

"Die Margarine-Fabrikation," von TH. BUDDINGER. Separat-Abdruck aus dem Organ für den Oel- und Fetthandel. 2nd edition. Verlag N. Besselich. Pp. 16. Trier, 1910.

ARTIFICIAL BUTTER, MARGARINE

BUTTER fat is a mixture of the glycerides (both simple triglycerides and mixed glycerides) of acetic, butyric, caproic, caprylic, lauric, myristic, palmitic, stearic, arachidic, and oleic acids. It also contains small amounts of cholesterol and natural colouring matters (lactochromes). The average proportions of the acids are as follows: Stearic acid, 0·49 per cent.; palmitic acid, 18·23 per cent.; myristic acid, 11·08 per cent.; lauric acid, 16·4 per cent.; oleic acid, 36·1 per cent.; caproic, caprylic and capric acids, 3·23 per cent.; butyric acid, 6·13 per cent.; glycerol, 12·5 per cent. Cow butter consists of fat, 83-91 per cent.; water, 7·5-13·75 per cent.; casein, 0·5 per cent.; milk sugar, 0·3 per cent.; ash, 0·3 per cent.; salt, 1-2 per cent.

Since glycerides of the same fatty acids are present in varying amounts in many other fats and fatty oils, the problem which confronts the margarine manufacturer is the blending together of these fats so as to produce a substance having the same chemical composition as butter. Chemically this could be done by separating pure glycerides from the various fats (making them artificially if necessary), and then blending them together in the exact proportions in which they occur in butter fat. On the large scale this operation is quite impracticable on account of cost, so that the art of the margarine manufacturer consists in utilising the fats ready to hand, and blending them together in such proportions as most closely simulates the natural product. This has been so successfully achieved that many of the margarines now on the market resemble butter so closely in physical and chemical properties that the analyst has often very great difficulty in deciding whether a sample consists of true or artificial butter. There can be little doubt that ultimately a margarine will be produced having almost exactly the same constituents as natural butter, and therefore indistinguishable from it either by chemical tests or natural flavour.

Manufacture of Margarine

The following ingredients are used in various percentages according to the quality of the margarine it is desired to produce: oleo oil, neutral lard, coco-nut oil, earth-nut oil, sesamé oil, and cotton-seed oil. The refining of oils has become so perfect of late, through the application of the so-called American "Wesson Process," that the oils used are now absolutely flavourless and neutral. About 50 per cent. of carefully soured cream or milk is churned through the above-named fats, and these, being quite tasteless, adopt the milky and buttery flavour of the soured cream. To the highest grades up to 10 per cent. of pure butter fat (the highest percentage allowed by law) is still added, which brings the quality so near the real article that even experts often cannot detect any difference.

All countries nowadays make about the same blends. Generally speaking, one can say that higher grades contain about 10 per cent. of oil, 70 per cent. of oleo oil, and 20 per cent. of coco-nut oil, whilst lower grades contain up to half oil and half animal fats.

Process of Manufacture.—The milk after a searching bacteriological and qualitative examination is passed through the separators, where the cream is separated from the milk. The cream is either churned into butter, or, what is usually more profitable, sold as cream. The separated milk is at once pasteurised (*i.e.*, heated to a temperature a little below its boiling point in order to destroy bacteria) and immediately cooled to nearly freezing point, remaining at this temperature until required for the "souring tanks," when it is again warmed to a moderate temperature suitable for the souring culture, which is then added. The souring culture is prepared in the bacteriological laboratory in the most careful manner, since the buttery flavour of the whole yield of margarine is dependent upon this. The milk is then allowed to "ripen" in a series of great open tanks, in which the milk is gently worked to and fro during the process; the floor is of concrete, and clean water is kept flowing over it, while the walls of the room are of glazed white ware, so that at this stage the danger of introducing foreign bacteria is minimised.

The milk thus prepared is now mixed in suitable quantities with the above-mentioned animal and vegetable oils in suitable proportions, and the mixture is thoroughly churned for not more than one hour in a suitable machine. The temperatures vary from 20°-45° C. The higher the quality the lower the churning temperature, the object being to retain as much as possible of the delicate milk flavour, which a high temperature largely destroys. In this way the product gets the characteristic smell and taste of butter.

Then, the property of butter to brown and froth being due to casein and milk-sugar, suitable proportions of these, or sometimes also of "Elaine," extracted from yoke of eggs, are added to high grade margarines.

In the churning machines the ingredients are thoroughly beaten into an emulsion or cream, the mixture being pulverised into single globules such as butter fat forms in milk, the process being regulated if necessary by means of steam or ice water sent through the steam jacket with which the churn is provided. The mass is then run out into large wooden tanks (sometimes coated with marble slabs, cleanliness being everywhere of the utmost importance). While running out in a thin stream from the churns the fluid margarine is met by a high-pressure jet of cold water, which pulverises the margarine, so that the disintegrated globules after solidifying resemble butter granules very closely.

This method of chilling the margarine has always been a source of dissatisfaction to the manufacturer, as it is impossible to perfectly control it, and even under the most favourable circumstances it did not give the best results for the following reasons:—

1. The milk serum in the emulsion is partly replaced by water.
2. Part of the souring culture is washed out, this resulting in an irregular and insufficient development of the souring ferment during the subsequent operations.
3. The chilling not being carried out at a sufficiently low temperature, the finished margarine is always of a softer and more greasy texture than butter.

To remedy these defects a process has recently been patented by Mr E. Schou which does away with the water cooling. The emulsion as it leaves the churn is spread out into very thin layers of about one-fiftieth of an inch in thickness on two large drums, revolving at the same speed but in opposite directions. These drums are cooled down by means of refrigerated brine to a temperature of about − 10° C., so that the very thin layers of emulsion immediately crystallise on the drums, and *while retaining the whole of the milk serum*, are scraped off in thin flakes, and treated as subsequently described. The advantages of this method are very great, viz. :—

1. The whole of the milk serum and souring culture being retained, a perfect control of the flavour of the margarine is secured.

2. Through the more effective cooling, the texture of the margarine becomes firm and at the same time pliable, and both to the naked eye and under the microscope it is hardly to be distinguished from butter.

The process has been worked for some time by one of the largest firms of margarine manufacturers in this country with such success that the best qualities of margarine thus prepared are equal, if not superior, to the best qualities of pure butter.

The solidified margarine is now removed in wooden wagons to the fermenting rooms, where the excess of water is allowed to drain off, and the souring culture in the milk allowed to develop and flavour the whole mass of margarine. After "ripening" for a sufficient time, the mass is transferred to large kneading machines in order to squeeze out the excess of water and obtain a homogeneous mass. Salt may be kneaded in to taste, together with colouring matter to produce the fine yellow colour characteristic of butter. Many colouring substances are sold (some even being aniline dyes).

Two harmless **colouring mixtures** much used are these :—

(*a*) Orlean, 80 parts ; curcuma root (turmeric), 80 ; olive oil, 240 by weight ; saffron, 1 part mixed with alcohol, 5 parts by weight. Macerate the orlean and turmeric with olive oil, express, make up the weight of the filtered liquid to 240 parts by weight with olive oil ; then add the filtered saffron-alcohol extract, stir, and expel the alcohol by heating the mixture.

(*b*) Moisten 30 parts of finely powdered alum with 3 parts of turmeric extract, spread out and dry the powder in a warm place ; then pulverise finely, and store, protecting the product from the light. A pinch of the powder added to a churnful of milk or cream before the churning imparts a beautiful golden colour. The turmeric extract is made by adding 1 part powdered turmeric to 5 parts alcohol, and macerating together for about a week ; then filtering. After the kneading the margarine is moulded into lumps, etc., ready for the market.

As a food, margarine is little (if at all) inferior to butter, and being prepared from the freshest and purest materials, is usually cleaner than butter as prepared in the dairy.

Distinctive Tests between Butter and Margarine (see also pp. 166, 167).—1. The Reichert-Meissl value (see under **Fat Analysis**) for butter is very large (20-33 cm.). That of most fats ranges from 0·5-1·5 cm. (coco oil, 7-8). Margarine makers now often add glycerides of volatile acids, so as to obtain the same number as with true butter.

2. The saponification value of butter is high (221-233), that of other fats low. The addition of coco-nut oil to the margarine raises its saponification value to that of butter.

3. The refractive index of butter is 1·4590-1·4620 at 25° C. (butyro-refractometer scales, 49·5-54). That of margarine is 1·4650-1·4700 (58·6-66·4 butyro-refractometer divisions). Coco-nut oil lowers the refractive index of margarine to that of butter.

4. True butter fat contains less than 1 per cent. of stearic acid. Most margarines contain 10-20 per cent., and even more. For other tests see under **Butter**.

S. H. Blichfeldt (*Journ. Soc. Chem. Industry*, 15th July 1910, p. 792, vol. xxix.) has devised a process for the estimation of **butter** and **coco-nut fat** in margarine.

The fat is saponified by a mixture of aqueous potash and glycerol, and the fatty acids are liberated by acidification with sulphuric acid. The resulting mixture is distilled in a specially designed apparatus, made by Becker, London.

The distillate is treated with an excess of decinormal soda solution and transferred to a 200 c.c. measuring flask. The total volatile acids are determined by titrating back with decinormal sulphuric acid. The neutral soap solution is now treated with excess of decinormal silver nitrate solution, and 10 per cent. of solid sodium nitrate is dissolved in the liquid in order to salt out all the sparingly soluble silver salts. After making up to 200 c.c., the precipitated silver salts are filtered off, and the excess of silver nitrate is determined volumetrically in the filtrate. The volatile fatty acids are thus determined as soluble and insoluble silver salts.

The ratios of soluble to insoluble silver salts, derived from butter and coco-nut fats respectively, differ considerably from one another, and afford a ready means of determining these substances in presence of one another.

The following table illustrates this:—

	Total Volatile Fatty Acids.	Soluble Silver Salts.	Insoluble Silver Salts.
Butter	32	29	3
Coco-nut oil	20	4	16
Palm-kernel oil	15	3	12

Suet substitutes consist of a mixture of suet (tallow) and cotton-seed oil or cotton-seed stearin.

Lard substitutes are mixtures of lard or "lard stearin" (p. 14), with cotton-seed stearin, maize oil, coco-nut oil, and other similar oils. In Germany such substitutes are heated with onions and condiments, and sold as cooking fat (*bratenfett*). "Hardened" oils now enter into the composition of some lard substitutes.

Margarine Cheese is made from milk from which the cream has been removed, and to which margarine fat has been added. Otherwise the operation is just like cheese-making in the ordinary way. In 1910 about 1,600 cwt. (value, £2,500) were imported into Great Britain.

Statistics of the Butter and Margarine Trades.—The following figures relate to the output of butter, cheese, and margarine of the **United Kingdom** for the year 1907 (First Census of Production, 1907):—

TABLE I.—OUTPUT

NOTE.—*The figures in this Table are given to the nearest thousand in each case*

	England and Wales.	Scotland.	Ireland	United Kingdom.
	Quantity.			
	Cwt.	Cwt.	Cwt.	Cwt.
Butter, made or blended	408,000	14,000	678,000	1,100,000
Cheese	53,000	20,000	2,000	75,000
	Imp. Galls.	Imp. Galls.	Imp. Galls.	Imp. Galls.
Cream, sold	750,000	214,000	134,000	1,098,000
	Cwt.	Cwt.	Cwt.	Cwt.
Margarine (including all kinds of artificial or imitation butter)	745,000	71,000	65,000	881,000
Other milk products, bacon, and packing cases		(*Recorded by*	*Value only.*)	
	Value.			
	£	£	£	£
Butter, made or blended	1,206,000	83,000	3,551,000	5,840,000
Cheese	155,000	32,000	6,000	193,000
Cream, sold	291,000	65,000	42,000	398,000
Margarine (including all kinds of artificial or imitation butter)	1,759,000	181,000	154,000	2,094,000
Other milk products, bacon, and packing cases	1,293,000	33,000	313,000	1,639,000
Total value	5,704,000	394,000	4,066,000	10,164,000

TABLE II.—COST OF MATERIALS USED, SHOWN IN RELATION TO VALUE OF OUTPUT

NOTE.—*The figures in this Table are given to the nearest thousand in each case*

	England and Wales.	Scotland.	Ireland.	United Kingdom.
I. Cost of materials used	£ 4,960,000	£ 326,000	£ 3,710,000	£ 8,996,000
II. Value of output	5,704,000	394,000	4,066,000	10,164,000
III. Value of output *less* cost of materials used	744,000	68,000	356,000	1,168,000

The following statement shows the particulars furnished respecting the output of such factories and workshops, and is free from duplication:—

	1907. Quantity.	1907. Value.
	Cwt.	£
Butter, made or blended	1,100,000	5,840,000
Cheese	75,000	193,000
	Imp. Gallons.	
Cream, sold	1,098,000	398,000
Margarine (including all kinds of artificial or imitation butter)	Cwt. 881,000	2,094,000
Other milk products, bacon, and packing cases	Recorded by value only	1,639,000

The total value of the above-mentioned products is £10,164,000.

The butter included above is partly made and partly blended, and consequently all firms receiving schedules were asked to make a voluntary statement showing separately the quantities made and blended. Firms with an output of 996,000 cwt., or over 90 per cent. of the total quantity included in the returns, stated that they made 482,000 cwt. of butter (37,000 cwt. in England, 9,000 cwt. in Scotland, and 436,000 cwt. in Ireland), and blended 514,000 cwt. (350,000 cwt. in England and 164,000 cwt. in Ireland). It appears probable that the bulk of the butter bought for blending was made in the United Kingdom by farmers from whom it was purchased.

The firms making returns to the Census Office included in their statements of output a comparatively small quantity of whole milk, the selling value of which has been deducted from the value of the output and from the cost of the materials used. The cost of materials used, as given in Table II. is accordingly understated by the amount of the profit on the sale of the whole milk, but the error so introduced is insignificant.

Net Output.—The net output of the factories and workshops covered by the Tables on pages 176, 177 (whose gross output was valued at £10,164,000) was £1,168,000, that sum representing the total amount by which the value of the products of such factories and workshops exceeds the cost of the materials used in their manufacture. The actual cost of the materials used by those factories and workshops, taken as a whole, was about £8,996,000.

The net output per head of persons employed in the censal year (1907) was a little over £125.

Persons Employed.—The average number of persons employed on the last Wednesday in January, April, July, and October, in 1907, in the factories, together with the number ordinarily employed in the workshops, covered by the Tables on pages 176, 177, is returned as 9,333, viz., 7,754 wage-earners and 1,579 salaried persons, the total number being distributed by age and sex as follows:—

Males:—		Females:—	
Under 18	700	Under 18	435
Over 18	6,607	Over 18	1,591

So far as regards Ireland, the number of persons engaged in auxiliary creameries are not included in the foregoing figures, which cover in the main only persons engaged in central creameries and in butter-blending and margarine factories. It is understood that the persons employed at auxiliary creameries are not in all cases engaged during their full time in the separation of cream.

The amount of **margarine** imported into the United Kingdom is given by the following figures :—

	1906.	1910.	Value in 1910.
	Cwt.	Cwt.	
Margarine - - - -	1,101,900	1,120,800	£2,900,000
„ cheese - - -	1,200	1,600	2,500
Imitation lard - - -	231,000	275,000	600,000

Exported was 7,000 cwt. (value £17,000), in 1910, of **margarine** ; and 2,700 cwt. (value £6,600) of imitation lard.

The United States in 1910 exported 74,556,000 lbs. of lard substitutes (value, $6,887,000), and 3,418,000 lbs. of oleo-margarine or imitation butter (value, $350,000).

The following are recent statistics of imports and exports :—

IMPORTS OF MARGARINE INTO THE UNITED KINGDOM

Articles and Countries whence Consigned.	Quantities.			Value.		
	1912.	1914.	1916.	1912.	1914.	1916.
Margarine, that is to say, any article of food, whether mixed with butter or not, which resembles butter and is not milk-blended butter. (See Butter and Margarine Act, 1907, and Sale of Food and Drugs Act, 1899.) (I. C (1)):	Cwt.	Cwt.	Cwt.	£	£	£
Norway - - - - -	8,463	4,977	2,521	21,278	13,055	8,674
Netherlands - - -	1,314,505	1,502,576	2,738,343	3,396,927	3,896,375	8,917,714
Belgium - - - - -	856	566	...	2,008	1,486	...
France - - - - -	19,804	13,389	9,800	75,940	50,037	50,551
United States of America -	7,216	5,969	2,165	13,488	12,126	5,948
Other Foreign Countries -	1,583	1,671	37	4,404	4,118	120
Total from Foreign Countries	1,352,427	1,529,148	2,572,866	3,514,045	3,977,197	8,983,007
Canada - - - - -	...	26	...	...	52	...
Other British Possessions -	...	45	...	...	112	...
Total from British Possessions	...	71	...	...	164	...
Total - -	1,352,427	1,529,219	2,752,866	3,514,045	3,977,361	8,983,007
Margarine Cheese (I. C (1)):	Cwt.	Cwt.	Cwt.	£	£	£
United States of America -	295	...	...	767	...	..
Other Foreign Countries -	...	...	...	...	...	...
Total - - -	295	...	...	767	...	...

EXPORTS OF MARGARINE FROM THE UNITED KINGDOM

Articles and Countries whence Consigned.	Quantities.			Value.		
	1912.	1914.	1916.	1912.	1914.	1916.
Margarine (including all kinds of artificial or imitation butter) (I. C):	Cwt.	Cwt.	Cwt.	£	£	£
Denmark (including Faröe Islands)	1,245	979	401	3,174	2,604	1,393
Iceland and Greenland	1,175	712	427	3,105	1,807	1,284
Netherlands	1,825	23	150	3,802	69	446
Belgium	1,613	177	40	5,998	593	154
France	1,267	81	1,379	5,854	410	5,198
Egypt	1,504	1,301	...	4,786	4,119	...
Panama	1,037	320	...	2,895	704	...
Other Foreign Countries	1,308	562	198	3,812	1,824	793
Total to Foreign Countries	10,974	4,155	2,595	33,426	12,130	9,268
Channel Islands	1,685	2,209	4,320	5,885	8,002	16,689
Gibraltar	1,880	1,514	1,731	6,274	5,271	6,525
Malta and Gozo	936	1,168	1,828	2,733	3,752	6,046
Egypt	...	...	414	...	...	1,633
Cape of Good Hope	2,604	2,052	3,424	7,077	5,533	11,891
Natal	1,820	1,759	1,028	4,244	4,402	3,249
Transvaal	970	885	750	2,310	2,158	2,325
Australia	1,308	382	723	3,388	1,259	3,027
British West India Islands	2,861	2,330	1,618	8,650	6,837	6,176
Other British Possessions	1,625	2,488	3,245	4,744	6,349	11,497
Total to British Possessions	15,689	14,787	19,081	45,305	43,563	69,058
Total	26,663	18,942	21,676	78,731	55,693	78,326

CHAPTER XIV

Manufacture of Fatty Acids and Candles

CHAPTER XIV

MANUFACTURE OF FATTY ACIDS AND CANDLES

LITERATURE

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CANDLES are commonly composed of free fatty acids such as stearic and palmitic acids. Hydrocarbons such as paraffin wax or ceresin are now very largely used, either alone or (more usually) mixed with fatty acids. Certain waxes, such as beeswax, carnaüba wax, spermaceti, etc., are employed in making some of the more expensive sorts of candles, while ordinary tallow enters into the composition of some of the inferior qualities.

Obviously good candle material must burn without smoke or smell, must not soften and bend under usual conditions of temperature, and when melted, must form a fluid which can be readily drawn up by the wick. Tallow is soft and burns with a foul smoky flame, and so is only used for the cheaper kinds of candles. Some of these objections apply to inferior sorts of paraffin.

Preparation of Fatty Acids for Candle-Making (also for Soap-makers).—The fats are saponified by several processes:—

Saponification by Lime (de Milly's Process).—Some 6,500-7,500 lbs. of fat are placed in a copper digester and 1-3 per cent. of lime (or magnesia) and a little water is added.* Saturated high-pressure steam is then turned on, and the whole is heated for six to eight hours with steam at a pressure of 8-10 atmospheres. Under these circumstances a temperature of over 176° C. prevails within the digester, and the fat is almost completely hydrolised into glycerol and fatty acids as follows:—

$$\underset{\substack{\text{Tristearin,}\\ \text{890 parts.}}}{C_3H_5(O.CO.C_{17}H_{35})_3} + \underset{\text{Water.}}{3H_2O} = \underset{\substack{\text{Glycerol,}\\ \text{92 parts.}}}{C_3H_5(OH)_3} + \underset{\substack{\text{Stearic acid,}\\ \text{852 parts.}}}{3C_{17}H_{35}COOH}$$

At the same time the lime present is turned into an insoluble calcium salt, thus:—

$$\underset{\text{Tristearin.}}{2C_3H_5(O.CO.C_{17}H_{35})_3} + \underset{\text{Lime.}}{3Ca(OH)_2} = \underset{\text{Glycerine}}{2C_3H_5(OH)_3} + \underset{\substack{\text{Calcium stearate}\\ \text{(insol. lime soap).}}}{3(C_{17}H_{35}.CO.O)_2Ca}$$

---

* Superheated water alone at a temperature of over 200° C. (15-20 atmospheres pressure) is capable of almost completely hydrolising fats. The presence of lime, however, allows the temperature and pressure required for saponification to be greatly reduced.

A modern digester consists of a copper boiler (iron discolours the fatty acids) 5·6 ft. in diameter and 18-30 ft. high (Fig. 71). The contents are agitated either by paddles or rotating spiral screws.

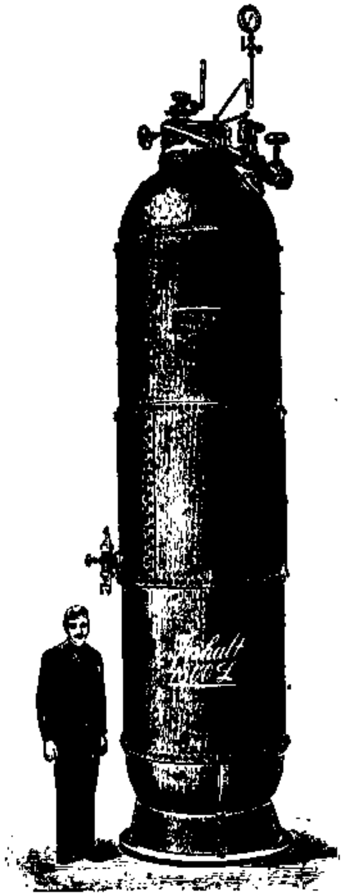


FIG. 71.—Copper Digester for the Manufacture of Fatty Acids by de Milly's Process.

The glycerol collects in the water underneath the oily layer of fatty acids. From time to time a sample of fat is withdrawn and analysed, and when the process of saponification is thus found complete enough, the mass is allowed to stand until the separation into two layers—fatty acids above and glycerine ("sweet") water below—is complete. The two layers are then pumped off into separate vessels.

The fatty layer is now boiled up with steam, and sufficient sulphuric acid added to decompose the lime soap contained in the fatty acids, thus:—

$$\underset{\text{Calcium stearate.}}{(C_{17}H_{35}CO.O)_2Ca} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Calcium sulphate.}}{CaSO_4} + \underset{\text{Stearic acid.}}{2C_{17}H_{35}COOH}$$

On standing, the calcium sulphate separates as a sludge at the bottom of the watery layer, while the fatty acid forms an oily layer above: the two layers are separated.

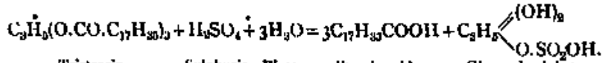
The further treatment of the fatty acids depends upon the quality of the fat used for saponification.

If the best tallow or fatty oils have been employed, the fatty acids thus obtained may be white enough for direct pressing and conversion into candles as described below, while the glycerine water may be worked up for good quality glycerol as described under Glycerol.

Usually, however, the best sorts of tallow are used for edible purposes, and the candle or soap maker works with inferior dark coloured fats, which yield fatty acids too dark for direct use in candle-making. Consequently, the fatty acids so obtained are either distilled with steam, as described below, or else the neutral fats are treated with concentrated sulphuric acid (acid saponification) in a manner we will now describe.

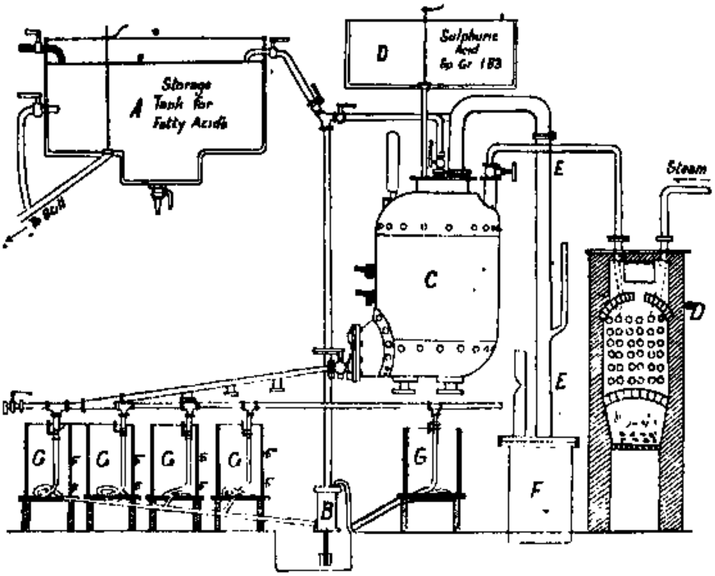
Saponification of Fats by Means of Sulphuric Acid.—This process is usually used for inferior fats obtained from garbage, putrid bones, etc. The fatty acids from the lime saponification process (from which the glycerine has already been extracted) are often subjected to this process in order to slightly increase the yield of candle material, since the sulphuric acid turns the fluid oleic acid into oxystearic acid, a hard white solid capable of being utilised in candle-making; thus, while the lime saponification process alone yields 45-47 per cent. of solid fatty acids, the acid saponification process yields 55-63 per cent., with a slightly lower melting point.

The process is carried out as follows (Fig. 72): The dark coloured fat is melted in an iron tank by means of a closed steam coil, and heated until most of the water present is expelled. Next, the melted fat is forced by means of the pump B into a copper boiler C, and 3-6 per cent. of concentrated sulphuric acid of sp. gr. 1·83 run in from the lead-lined tank D. The whole is heated for five to six hours at 130° C. by means of a closed copper coil, through which superheated steam from the superheater D is passed. The sulphurous fumes arising from the action of the acid on the fat are pumped away through EE by means of a water jet contained in the vertical pipe, which discharges into F. A complicated action ensues; the hot, strong acid attacks the fat, thus:—



$$C_3H_5(O.CO.C_{17}H_{35})_3 + H_2SO_4 + 3H_2O = 3C_{17}H_{35}COOH + C_3H_5\begin{matrix}\diagup (OH)_2\\ \diagdown O.SO_2OH.\end{matrix}$$

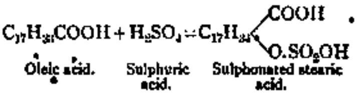
Tristearin. Sulphuric acid. Water. Stearic acid. Glyceryl sulphate.



PLANT FOR ACID PROCESS OF FAT SAPONIFICATION

FIG. 72.

The hot water at the high temperature employed also saponifies the fat into glycerol and free fatty acid, so that instead of the theoretical 11 per cent. sulphuric acid required according to the above equation, in practice only some 3-4 per cent. are necessary. The fats blacken considerably owing to the destruction of tissues and membranes present by the concentrated sulphuric acid. At the temperatures employed the fatty acids themselves are scarcely affected. If, however, the temperature is allowed to rise too much, the sulphuric acid finally attacks them, converting them into sulphonic acids. Some of the glycerol is destroyed. Part of the oleic acid present is converted into an unstable sulphonic acid, thus:—*



$$C_{17}H_{33}COOH + H_2SO_4 = C_{17}H_{34}\begin{matrix}\diagup COOH\\ \diagdown O.SO_2OH\end{matrix}$$

Oleic acid. Sulphuric acid. Sulphonated stearic acid.

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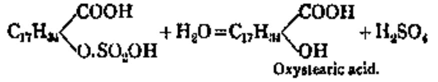
[*] According to Lewkowitsch (*Journ. Soc. Chem. Ind.*, 1897, 392) sulpho-hydroxystearic acid is formed.

The subsequent boiling with water decomposes this sulphonic acid into oxystearic acid, thus:—



$$C_{17}H_{34}\left<\begin{matrix}COOH\\ O.SO_2OH\end{matrix}\right. + H_2O = C_{17}H_{34}\left<\begin{matrix}COOH\\ OH\end{matrix}\right. + H_2SO_4$$

Oxystearic acid.

And this, in the subsequent distillation of the fatty acids, is partially converted into a solid isomeride of oleic acid, called iso-oelic acid, $C_{17}H_{33}COOH$, M.P. 44° C. There are also formed at the same time lactones and hydrocarbons of unknown constitution. The net result of the operation is an increase in the amount of solid matter capable of being used for candle material.

The action being completed, the tarry matter at the bottom of the boiler is run off, and the fatty acids boiled with water in a series of lead-lined tanks (G, G, G), the heating being effected by open steam coils contained in them. Finally, the fatty acids, now washed free from sulphuric acid, are pumped up into the storage tank A, from whence they are run into the steam still for a final purification by distillation, as described below (p. 188).

Formerly no attempts were made to recover the glycerol, and statements are even now published in standard works stating that the glycerol is almost completely destroyed. Glycerol, however, is too valuable a product to throw away, and it is now extracted with little loss from the acid and aqueous liquors run off from the fatty acids (see under Glycerol).

Twitchell's Process of Saponification.*—When concentrated sulphuric acid is allowed to act on a mixture of benzene and oleic acid at a temperature below 30° C., the following action takes place:—

$$\underset{\text{Benzene.}}{C_6H_6} + \underset{\text{Oleic acid.}}{C_{18}H_{34}O_2} + \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{H_2SO_4} = \underset{\text{Sulpho-benzene-stearic acid.}}{C_6H_4(HSO_3)(C_{18}H_{35}O_2)} + \underset{\text{Water.}}{H_2O}.$$

The sulpho-benzene-stearic acid may be separated by washing the viscous oil thus produced with water. In place of benzene we may employ naphthalene or phenol and obtain similar compounds, naphthalene yielding, for example, sulpho-naphthalene-stearic acid, $C_{10}H_6(HSO_3)C_{18}H_{35}O_2$.

This new series of fatty aromatic acids has the remarkable property of readily hydrolising fats into glycerol and fatty acids when boiled with them. The fat, previously purified by boiling with dilute sulphuric acid in a lead-lined wooden tank A, is pumped into a lead lined wooden tank B, provided with a closely fitting cover, about one-third of its weight of distilled water from D is run in, and 0·5-1 per cent. of the sulpho-benzene-stearic acid (or similar body) added. Live steam is then driven through the liquid by means of the open coil C, and the boiling continued for twelve to twenty-four hours, when the saponification will be complete. During the boiling no air must be allowed to come into contact with the fat or a dark coloured product will result; hence the lid of the saponifying tank must fit practically air-tight; also a small steam-pipe should be fixed in the top of the vat, so that during all pauses in the process any air is prevented from coming into contact with the fat and causing discoloration of the fatty acids. Finally, the mixture is allowed to settle; the fatty acids separate out as a clear oily layer above, and the glycerol water below. The glycerol water is drawn off into E, and the fatty layer boiled up again with some fresh water for another twelve to twenty-four hours, when all the glycerol is extracted. At this stage a little barium carbonate mixed with water (1 part barium carbonate to 2,000 lbs. of stock) is added to B in order to neutralise acid in the fat, and the boiling with steam resumed until the fat is neutral to methyl orange. Finally, the mass is allowed to settle, and the glycerol water drawn off first, and then the fatty acids, which are now ready for use.

The glycerol water in E—amounting to about 66 per cent. of the volume of fat—is neutralised by a little milk of lime contained in H, the sediment allowed to settle, and the clear glycerol water pumped into G, passing if not quite clear through the cloth filter in F. From G the glycerol may be passed to the evaporators to be boiled down and distilled.

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* Eng. Pat., 4,741, 1898.

Advantages of the New Process.—1. The great simplicity of apparatus and operations.

2. The glycerol water drawn off from the fat is very rich in glycerol, yielding when boiled down a very pure product at little cost.

The **Disadvantage** is the tendency to produce dark coloured products. An apparent improvement on Twitchell's original reagent, both in respect to the lighter colour of the fatty acids produced and the smaller amount necessary for saponification, is the **Dartring** saponifier (English Patent 749, 1912; German Patent, August 1911, V. 9,847), placed on the market by the Vereinigte Chemische Werke A.G., Charlottenburg, and Geo. Haller & Co., of London.

Other Processes of Saponification.—Colloidal metals (*e.g.*, platinum) readily hydrolise fats (see *Journ. Soc. Chem. Industry*, 1909, 611). The process promises to develop into a technically important one.

Enzymes contained in many seeds also readily and spontaneously hydrolise fats at ordinary temperatures into free fatty acids and glycerol. For further information see *Journ. Chem. Industry*, 1906 (25), p. 994 (Fokin); 1905 (24), 977 (E. Hoyer); 1904 (23), 327 (Nicloux). Nicloux states that the enzyme contained in 10 kilos of crushed castor seed which has been extracted with castor oil is able to decompose 1,000 kilos of fats and oils in twenty-four hours at ordinary temperatures. The fats are stated to yield excellent light coloured soaps.

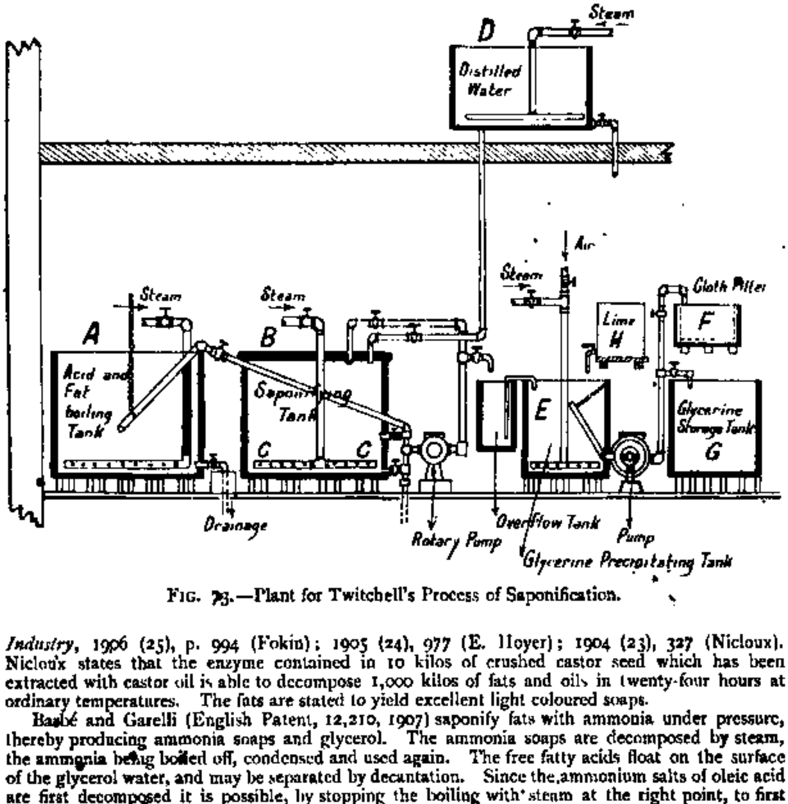

FIG. 73.—Plant for Twitchell's Process of Saponification.

Barbé and Garelli (English Patent, 12,210, 1907) saponify fats with ammonia under pressure, thereby producing ammonia soaps and glycerol. The ammonia soaps are decomposed by steam, the ammonia being boiled off, condensed and used again. The free fatty acids float on the surface of the glycerol water, and may be separated by decantation. Since the ammonium salts of oleic acid are first decomposed it is possible, by stopping the boiling with steam at the right point, to first separate the oleic acid, and then, by continuing the boiling, to separate the stearic and other acids.

In the Patent No. 9,758, 1908, they saponify with 0·5 per cent. of ammonia (which acts catalytically in the process) with steam at 130°-160° C. under 3-6 atmospheres for eight hours, and immediately separate the resulting very pure glycerol waters of 6°-7° Be. See also Patents 24,836 and 24,837, 1908.

Distillation of the Fatty Acids.—A typical still used for this purpose is shown in Fig. 74. The melted fatty acids are run from the storage tank M into the large copper still A, which is usually heated by direct fire to a temperature of about 260° C., while steam which has been heated to 260°-360° C. in the superheater B is blown through C, C into the mass of hot fatty acids. The fatty acids distil over into a series of copper condensers D, D, D, the liquid acids running from them down into copper coils E cooled by water in the wooden boxes K, K, K; from these coils they are drawn off, according to quality, into separate tanks. F is an auxiliary condensing arrangement, situated out of doors, for condensing the lighter portions of the redistilled tar. A water aspirator contained in F carries the fumes into the tank G; uncondensed vapours pass off through H, and are suitably disposed of.

About 18,000 lbs. of fat may be distilled continuously, the volume in the still being kept constant by the continual introduction of fat from the storage tank M in proportion as the volume in the still decreases during the distillation.

Palmitic acid first distils over, then stearic and oleic acids, and finally lactones and hydrocarbons. The first distillate (86-95 per cent. of the whole) is white in colour, and may be pressed at once for conversion into candle material. The later fractions, which are rich in bodies produced by the decomposition of the fatty acids—such as lactones and hydrocarbons—are returned to the storage tank M and redistilled. The black residue (liquid when hot, solid when cold) which finally remains in the still is known as **candle pitch**, and is run off through the outlet pipe *n*; it is used for making insulating material for electrical machines, for waterproof paper, as a lubricant, and as a constituent of black paints; it forms about 2 per cent. of the charge.

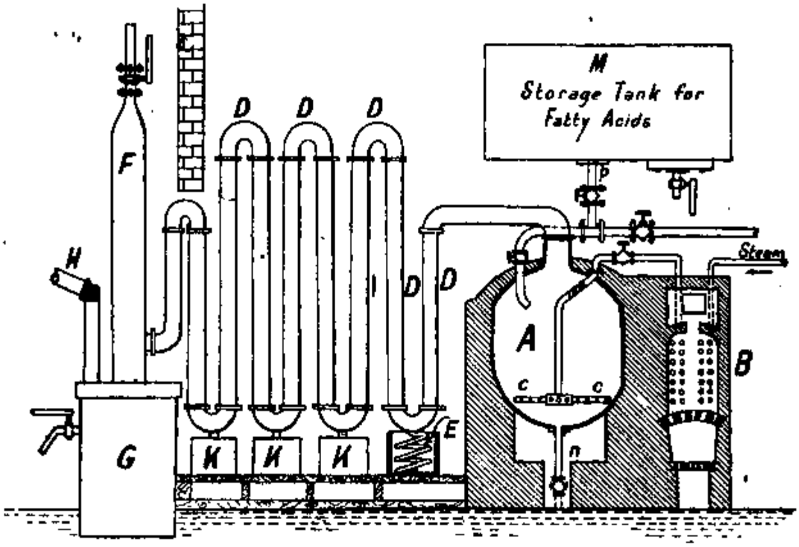

FIG. 74.—Plant for Distillation of Fatty Acids.

The United States in 1910 imported 4,263,000 lbs. of candle pitch (value, $70,000), of which 1,170,000 lbs. came from the United Kingdom.

Process of Pressing the Fatty Acids.—The fatty acids, purified as described above, are now run into a series of shallow tinned iron trays arranged one above the other in racks in a cooling room, which is artificially maintained at such a temperature that the fatty acids crystallise only very slowly during ten to twelve hours, so that the crystals of stearic and palmitic acid formed are large, and thus allow the liquid oleic acid, retained between them and forming the mother liquid out of which they crystallise, to be easily expelled by pressure.

The cakes of fatty acid thus obtained are wrapped in cloth and subjected to a hydraulic pressure of 250 atmospheres in the cold. Then they are pressed at a temperature of 60° C. in a "hot press," *i.e.*, one steam jacketed so as to allow the pressing to take place at this temperature. The white hard cakes thus obtained are remelted and clarified, when they are ready for use.

The expressed oleic acid, commonly called "**red oil**," is usually cooled, when a further separation of solid stearic and palmitic acid takes place. This is separated, and the mother liquid, consisting of impure oleic acid, is used as a wool oil or as a stock for textile soap.

Melting Points of the Fatty Acids.—These are important for their commercial valuation:—

	M.P.		M.P.
Oleic	4° C.	Elaidic	51° C.*
Oxystearic	84°-86° C.	Stearic	69° C.
Iso-oleic	44°-45° C.	Palmitic	62° C.

Process of Candle Moulding.—Candles consist of cylinders of wax or fatty acids surrounding a wick lying true in the centre in order to avoid unequal burning. These **wicks** are made of cotton threads loosely plaited together and soaked in a solution of boric acid, potassium nitrate or chloride, and ammonium chloride, sulphate, or phosphate. The plaiting causes the wick to curve when burning, and thus they burn away at the ends without causing the flame to smoke. The chemical solution vitrifies the ash of the wick, and the minute glassy particles dropping off from the bent wick leave the end free for the melted fat to ascend to the point where combustion is taking place. In the absence of this chemical treatment the wick burns off short in the flame and causes persistent guttering. Stearin or paraffin candles are moulded in special machines.

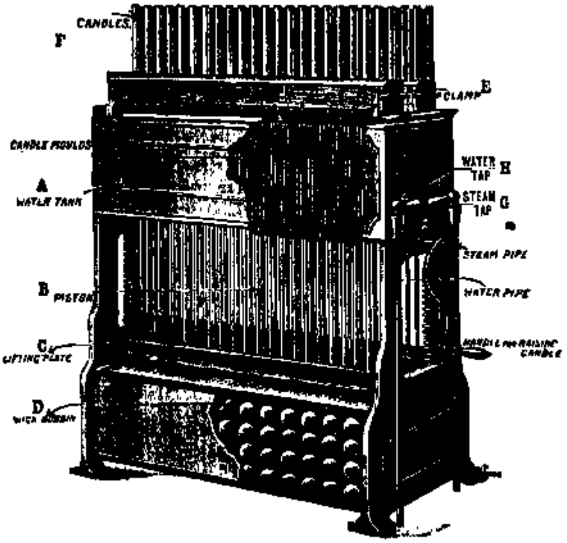

FIG. 75.—Modern Candle-Moulding Machine.
(From J. Calderwood's "Manufacture of Candles," p. 15.)

Fig. 75 represents an ordinary candle machine capable of moulding ninety-six candles simultaneously. It consists of a battery of moulds contained in an iron tank A, through which warm or cold water can be passed as desired in order to heat or cool the moulds. Each mould (the construction of which is shown in Fig. 76) is made of polished tin, sometimes backed by iron, and traversed by a piston which can be raised or lowered so as to force the candle out of the mould. The wicks are wound upon the bobbins D (Fig. 75), and pass up the piston rods B accurately through the centres of the candle moulds, shown in Fig. 76, and end in the candles from the previous "round," which are held in exact position in a special clamp. To use the machine hot water is first driven through the box containing the moulds so as to heat them to a suitable temperature; next the melted wax is poured into the trough, and not only completely fills the moulds, but leaves a sufficient surplus in the troughs to allow for contraction of material on cooling. Next the hot water is replaced by a stream of cold, which rapidly chills the moulds, and the candles solidify. The wicks of the candles held in the clamp above the trough are now cut, and the previous round of candles carried away for packing. The excess of candle material in the trough is now removed by means of a suitable tool, the emptied clamp replaced over the trough, and then, by operating the handle, the pistons D are pushed up the moulds, thus forcing out the candles into the holder or clamp E. The wicks are drawn up with the candles, so that, immediately after the withdrawal of the first lot of candles, the pistons are lowered and another charge of wax poured into the moulds. When the surplus material in the trough is sufficiently solid, the wicks above are cut by a special knife or scissors, and the clamps

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* Lewkowitsch gives 44·5° C. as the correct M.P.

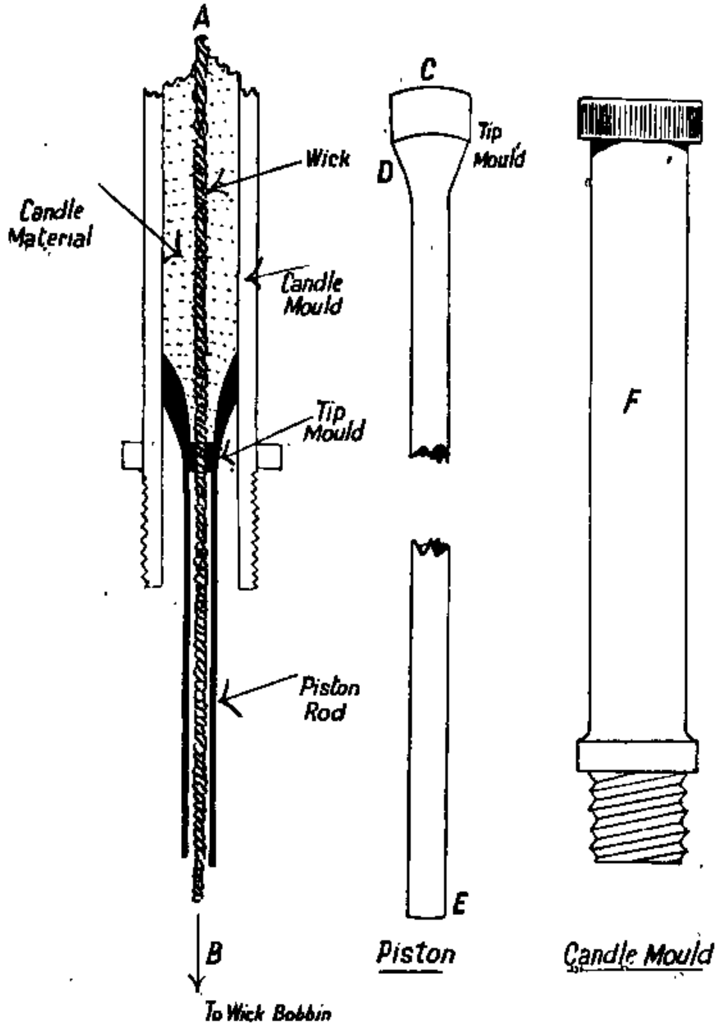


FIG. 76.—Section of Candle Moulds.

containing the candles are then lifted away, and the candles ejected into a rack or other convenient place. After the clamps have been replaced upon the machine the operation is continued until, ultimately, the bobbins D, which contain sufficient wick for several hundreds of candles, are emptied, when they are either rewound or replaced by others.

A great advance on these machines is represented by Cowles' "Multiple" candle-moulding machines, which enormously increase the output and effect a very great economy of labour, water, steam, and floor space; thus while by the use of a small candle machine such as that just described ninety-six candles can be produced at one operation, by the use of a multiple machine of the same size no less than 360 candles can be produced at one operation. The "Multiple" machine is capable of producing no less than 518 candles at one filling, filling three times an hour, and producing per week of fifty-five working hours no less than 90,000 candles. It is fitted with patent swing-over clamps for holding the ejected candles, depositing them in a V-shaped tray attached to the clamps.

"**Self-fitting**" **candles** have conical fluted ends by which they may be fitted into any candlestick without scraping or paper. Being tapered at both ends they cannot be produced in a single mould.

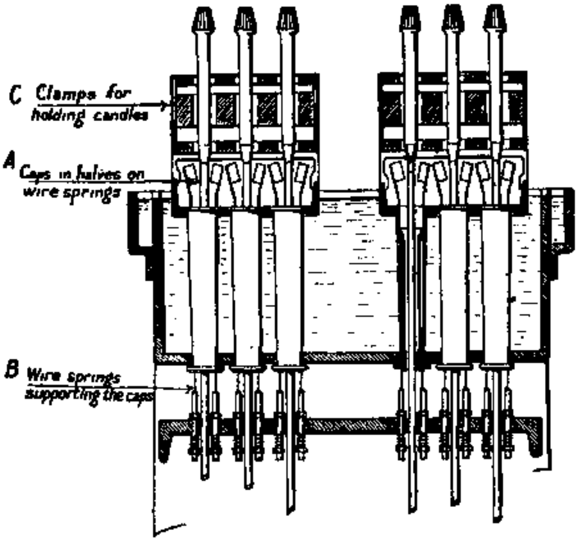

C Clamps for holding candles
A Caps in halves on wire springs
B Wire springs supporting the caps

Fig. 77.—Durpitt's Machine for Moulding Candles with Self-fitting Ends.
(By the courtesy of Price's Patent Candle Co.)

The arrangement used by Price's Patent Candle Company and patented by their Mr Durpitt is shown in the figure. The cap A, which forms a fluted conical butt, is in halves, each supported on wire springs B, which pass down recesses in the mould. When the candle is forced out of the mould these halved caps also rise a little, and springing apart they allow the enlarged butts of the candles to pass through; these are received in clamps C, and held in position over the centres of the moulds until the next lot of candles has solidified round the wicks, as in the ordinary "plain end" machines.

In some forms the conical ends are made by means of a movable top bed, fitted with moulds for these butts.

Usually a little paraffin is added to the stearin in order to render the wax less brittle. Also to paraffin candles varying amounts of stearin are added for similar reasons. Since low melting candle material is much cheaper than high melting material, candles are now manufactured with a thin exterior of any suitable high melting material, the interior being composed of the cheaper low melting material. Special machinery is required to perform the moulding, but the candles thus produced have the advantage of being very economical to manufacture, and not liable to gutter in burning, or cake together in packing, while the exteriors can be lettered for advertising purposes, or made of any desired colours, such colours not interfering with the combustion of the candle. **Wax** and **ceresin** candles are not moulded, because the wax at the moment of moulding shrinks away from the mould; also they stick to the form. Thick **altar candles** are made simply by pouring molten wax down a wick hanging vertically, and then rolling between boards. Smaller candles of the same material are made by drawing the wicks repeatedly through melted wax until of the proper size. By mixing beeswax with varying proportions of paraffin and stearic acid it is possible to mould it like ordinary candles.

Colouring Candles.—The candle material is usually coloured, before moulding, with organic colouring matter, the best sorts being those soluble in alcohol, since they affect least the burning power of the candle. The stearin is melted at 65° C., and the dye stirred in. The quantity varies between 0·05 and 0·01 per cent. of the weight of candle material. Mineral colouring matters cause the candles to burn badly, while many aniline dyes fade rapidly when in contact with the stearic acid. Good results are obtained with the following dyes: *Red*—sudan IV., flexin, rose bengal, rhodamin. *Yellow*—chinolin yellow, auramin. *Green*—acid green, Victoria green. *Blue*—indulin, Victoria blue, methyl violet.

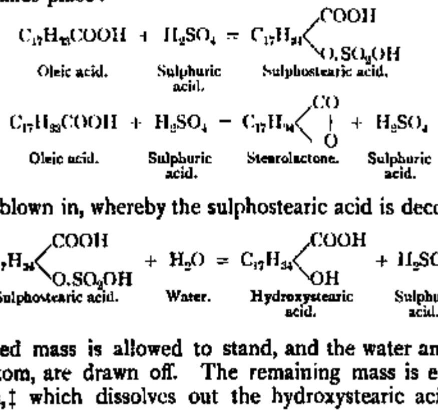
Transparent Candles for ornamental purposes may be made in a variety of ways. (1) If 100 parts of paraffin wax be melted at 80°-90° C. with 2 parts of beta-naphthol, a material is obtained which remains transparent on moulding. (2) Paraffin wax, 70, stearin, 15, and petroleum, 15, melted together, give a low melting point transparent candle material. (3) Paraffin wax, 90, stearin, 5, and petroleum, 5, give a higher melting point material somewhat less transparent than (2).

Statistics.—The value of candles imported into the United Kingdom in 1910 was 5,600 cwt. (value £14,500); exported were 292,000 cwt. (value £485,200).

The United States in the same year imported 160,000 lbs., value $26,000, and exported 5,215,000 lbs., value $244,000.

Manufacture of Candle Material from Waste Oleic Acid.—Oleic acid, expressed from the stearic and palmitic acids used in candle-making, is a viscid fluid quite useless as a candle material. Many attempts have been made to turn it into candle material, but only the first process described has met with any measure of commercial success.*

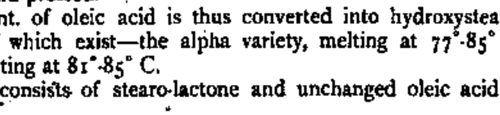
1. **The Conversion of Oleic Acid into Hydroxystearic Acid.**—Oleic acid is dissolved in distilled petroleum (60° Bé.), and cold concentrated sulphuric acid† run in, the temperature not being allowed to increase beyond 40° C. The following reaction takes place:



$$\underset{\text{Oleic acid.}}{C_{17}H_{33}COOH} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Sulphostearic acid.}}{C_{17}H_{34}\begin{cases}COOH\\ O.SO_2OH\end{cases}}$$

$$\underset{\text{Oleic acid.}}{C_{17}H_{33}COOH} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Stearolactone.}}{C_{17}H_{34}\begin{cases}CO\\ \ \vert\\ O\end{cases}} + \underset{\text{Sulphuric acid.}}{H_2SO_4}$$

Next, live steam is blown in, whereby the sulphostearic acid is decomposed, thus:—



$$\underset{\text{Sulphostearic acid.}}{C_{17}H_{34}\begin{cases}COOH\\ O.SO_2OH\end{cases}} + \underset{\text{Water.}}{H_2O} = \underset{\text{Hydroxystearic acid.}}{C_{17}H_{34}\begin{cases}COOH\\ OH\end{cases}} + \underset{\text{Sulphuric acid.}}{H_2SO_4}$$

The steam-heated mass is allowed to stand, and the water and sulphuric acid, sinking to the bottom, are drawn off. The remaining mass is extracted with hot petroleum naphtha,‡ which dissolves out the hydroxystearic acid. On cooling the petroleum the hydroxystearic acid separates out as a white mass, which is filtered, dried, and pressed.

Fifty per cent. of oleic acid is thus converted into hydroxystearic acid, two modifications of which exist—the alpha variety, melting at 77°-85° C., and the beta variety, melting at 81°-85° C.

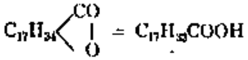
The filtrate consists of stearo-lactone and unchanged oleic acid; when it is distilled the unchanged oleic acid passes over, and part of the stearo-lactone is converted into oleic acid or iso-oleic acid, thus:—

---

* See "The Conversion of Oleic Acid into Candle Material," by Dr Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1908, p. 489.

† Zinc chloride has been also used for the purpose.

‡ U.S. Letters Patent, No. 772,129—N. M. Burton, patentee; Standard Oil Company, assignee—11th October 1904.



$$C_{17}H_{34}\left\langle\begin{matrix}CO\\ |\\ O\end{matrix}\right. = C_{17}H_{33}COOH$$

Stearo-lactone. Oleic acid.

The recovered oleic acid is again treated with sulphuric acid as above described, and a further quantity converted into hydroxystearic acid. It is claimed that by this process no less than 85-90 parts by weight of hydroxystearic acid are obtainable from 100 parts of oleic acid.

Hydroxystearic acid used alone is not a good candle-making material, although its melting point is high; but a mixture of 3 parts of the substance with 1 part of commercial stearic acid is used for stiffening paraffin wax candles.

For recent methods of converting oleic acid into hydroxystearic acid by treating with sulphuric acid, the reader may consult the following English patents:—

2,989, 1910.—**Dubovitz** treats benzine bone fat (1,465 kilos) with water (600 kilos) and MgO (8 kilos) in autoclave for eight hours; blows out, separates fatty acids and Mg soap from the glycerol water; dries fatty acids and Mg soap (1,412 kilos) and treats with 26 kilos of 92 per cent. H_2SO_4, for one hour; boils with H_2O. The iodine number was lowered from 44·9 to 33·2, giving 12·9 per cent. of solidified oleic acid.

10,466, 1904; 10,466A, 1904; and 19,988, 1905.—**Dreymann** treats the oleic acid with H_2SO_4, then esterifies the separated acids with methyl alcohol, and separates the pure acids by distilling *in vacuo* their methyl esters (which boil at a lower temperature than the fatty acids themselves), and decomposing them again into methyl alcohol and fatty acids and superheated steam.

24,836 and 24,837, 1908.—**Barbé, Garelli, and Paoli** treat the oleic acid with concentrated H_2SO_4, and convert the resulting anhydrides and lactones into acids by saponifying with ammonia (English Patents, 12,210, 1907; 9,758, 1908), decomposing the resulting ammonia soaps with cold water. The ammonium oleates are more soluble in cold water than the ammonium stearates, and consequently are drawn off in solution from underneath the stearic acid and stearic soaps, and a separation is thus effected of the oleic and stearic acids, the ammonia soaps being finally decomposed by boiling water, the ammonia recovered and used again, and the free fatty acid drawn off. They claim to obtain from oleic acid about 65 per cent. stearic acid melting at 70° C.

393, 1902.—**Sandberg** treats train oil with H_2SO_4 and nitrous acid. The nitrous acid converts the liquid oleic into solid elaidic acid, $C_{18}H_{34}O_2$.

2. **Conversion of Oleic Acid into Palmitic Acid.**—When oleic acid is fused with caustic alkali it is converted into palmitic acid, thus:—

$$\underset{\text{Oleic acid.}}{C_{18}H_{34}O_2} + \underset{\text{Caustic soda.}}{2KOH} = \underset{\text{Potassium palmitate.}}{KC_{16}H_{31}O_2} + \underset{\text{Potassium acetate.}}{KC_2H_3O_2} + \underset{\text{Hydrogen gas.}}{H_2}$$

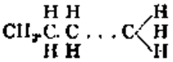
On acidifying the aqueous solution with dilute sulphuric acid, the palmitic acid is precipitated as a white crystalline mass. Candles made of palmitic acid manufactured by this method have actually appeared on the market, but the process was not commercially successful, the evolution of hydrogen making the manufacture dangerous, while the candles themselves possessed an unpleasant smell and greasy touch.

3. **Conversion of Oleic Acid into Stearic Acid.**—Oleic acid is an unsaturated acid, only differing from stearic acid by the absence of two hydrogen atoms. Several processes have been proposed for making oleic acid take up these two hydrogen atoms and become stearic acid according to the equation:—

$$\underset{\text{Oleic acid.}}{C_{17}H_{33}COOH} + \underset{\text{Hydrogen gas.}}{H_2} = \underset{\text{Stearic acid.}}{C_{17}H_{35}COOH}$$

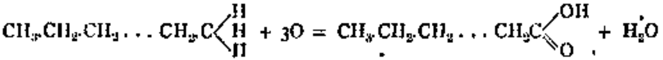
The processes are described in Chapter IX. on the **Hydrogenation of Fats.**

Production of Fatty Acids from Hydrocarbons and Mineral Oils.—A mineral oil may be presumed to possess the constitution



$$CH_3.\underset{H}{\overset{H}{C}}.\underset{H}{\overset{H}{C}}\ldots C\begin{matrix}H\\H\\H\end{matrix}$$

By absorbing oxygen it is theoretically possible to transform the substance into a fatty acid. Thus:—



$$CH_3.CH_2.CH_2\ldots CH_2.C\begin{matrix}H\\H\\H\end{matrix} + 3O = CH_3.CH_2.CH_2\ldots CH_2C\begin{matrix}OH\\O\end{matrix} + H_2O$$

Mineral oil. Oxygen. Fatty acid.

This has been successfully achieved during the last few years by German and other chemists. The technical details of the process are at present a carefully guarded secret.

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Contributed by E. A. Alliott, B.Sc.

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PREFACE

In the present volume will be found a concise and practical account, based on actual experience, of the modern methods of dealing with animal and vegetable oils, including their extraction, refining, and analysis. A considerable amount of the information collected together here appears for the first time. Within the last few years very great changes have occurred in the methods of dealing with oils, and much new and ingenious machinery has been invented to overcome difficulties which previously appeared almost insurmountable. Great attention has been paid to the recovery of oil from waste materials of all sorts, and recent methods are given fully in the present volume. The subject of hydrogenation of fats is dealt with very fully in Chapter IX., and some of the details there published now appear for the first time in book form.

The Author must take this opportunity of thanking several practical men for valuable information and suggestions. He is much indebted to Mr Wilson, Manager of the C.W.S. Bone and Fat Works at Pontefract, for many valuable details; also to Mr Dunlop, Manager of the C.W.S. African Oil Works at Liverpool; and to Mr J. W. Brizell, Chemist to the above works, with whom the Author worked out and patented a refining process for coco butter.

Mr Schmitt, of the Waste Eliminator Co., of London, was kind enough to revise proofs of the section relating to oil recovery from waste material.

Mr E. A. Alliott, B.Sc., A.M.I.M.E., very kindly contributed Chapter III., on the recovery of oil from metal turnings—a subject in which he is a specialist—while Mr Flockton, of Messrs Manlove Alliott, of Nottingham, was kind enough to supply details of machinery used in treating various kinds of seeds and in refining oils.

The Author also wishes to acknowledge his indebtedness to Mr Alfred Mansfield, Director of the Oils and Fats Branch, Ministry of Food, London, for giving official sanction for the printing in full as appendices* to this book the two valuable Reports recently published by his department, namely, the "Report by the Committee of Analysts on Standard Methods of Analysis of Seeds, Nuts and Kernels, Fats and Oils, and Fatty Residues," and the "Report by the Committee of Analysts on Standards of Good Merchantable Quality."

Mr Fred A. Lass, of the North Shields Fish Oil and Guano Co., Ltd., supplied valuable information on Fish Oils and Guano.

Mr Pooley, Mr West, and others of Messrs Scotts & Son, of Kingsway House, Kingsway, London, supplied much valuable data relating to oil extraction plant.

To all these, and others too numerous to mention, the Author returns his best thanks.

The Author will be pleased to hear from practical men, industrial chemists, and manufacturers engaged in the oil trade, both as regards any difficulties they may encounter in their work, and also as regards any errors or serious omissions in the book; for in spite of every care being taken it is always possible that in every case the best process has not been described, or that errors have crept in. Suggestions for increasing the utility of the work will be especially welcomed.

MANCHESTER, *October* 1919.

APPENDIX I

MINISTRY OF FOOD

OILS AND FATS BRANCH

STANDARDS OF GOOD MERCHANTABLE QUALITY

REPORT BY THE COMMITTEE OF ANALYSTS.

MEMBERS OF THE COMMITTEE OF ANALYSTS

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(Chairman).
JOHN ALLAN, Esq.
G. H. APPLEYARD, Esq.
E. R. BOLTON, Esq.
J. L. BUCHANAN, Esq.
ALFRED SMETHAM, Esq.
E. W. VOELCKER, Esq.
W. ELLARD WOOLCOTT, Esq.
(Messrs A. Norman Tate & Co.).

Standards of "Good Merchantable Quality"

To the Director of Oils and Fats, Ministry of Food

COMMITTEE OF ANALYSTS

SIR,

1. In the terms of reference submitted to us by you at our first meeting on 13th November 1918, we were asked to arrange standard tests for all constants and all schedules for oil seeds, nuts and kernels, and oils and fats. We have already communicated to you the results of our deliberations on this point.

2. We now forward for your consideration our report on the two other terms of reference which we have interpreted as follows:—

   i. To determine the ingredients affecting the value of any of the scheduled articles.

   ii. To consider the usual limits of constants for good merchantable quality of the scheduled articles.

3. *Standards for Vegetable Oils.*—An Official Schedule for Vegetable Oils, home manufactured, good merchantable quality, was submitted to us embodying a blank schedule for the insertion of standards and constants under several headings. After due consideration we decided that although all these particulars are of interest to analytical chemists it would not be practically useful to insert the whole of these in a contract. We therefore decided to limit our recommendations to those characteristics which have an immediate bearing on the commercial value of the oil.

4. We recommend the following standards for oil of "good merchantable quality" on the understanding

   i. That such oils shall be free from foots and foreign matter. (A mere compliance with the standard prescribed does not furnish proof of purity.)

ii. That an allowance should be made to the buyer or the seller for any deviation from these standards.

The figures are based on records covering in some cases a considerable period of years, and have been selected as representing a fair average, and as tending to raise rather than lower the existing standard.

SCHEDULE

Oil of "Good Merchantable Quality" shall be free from foots or foreign matter, and shall conform to the following standards:—

OIL.	Percentage of Free Fatty Acids (Oleic, except where otherwise stated).	Percentage of Moisture not Exceeding.	Percentage of Unsaponifiable Matter.	Other Standards.
LINSEED OIL—				
Raw	2	0.25	1	Iodine value (Wijs), 185
Refined	2	0.25	1	,, ,, 185
COTTON OIL—				
Crude, Indian	2.5	0.25	1.5	... ...
,, Egyptian	4			
Technical } Refined }	0.3			
Common edible	0.3			
Fine edible	0.15			
GROUND-NUT OIL—				
Crude	4	0.25	1	... ...
Fine edible	0.15			
SESAMÉ OIL—				
Crude	3.5	0.25	1	... ...
Fine edible	0.15			
RAPE OIL—				
Crude	1	0.25	1	Specific gravity 0.915. Viscosity, Redwood Standard.
Technical } Refined }	1			
Fine edible	0.1			
PALM-KERNEL OIL—				
Technical	5 lauric	0.25	1	... ...
Fine edible	0.1 ,,			
CASTOR OIL—				
Pharmaceutical	1	0.25	1	Specific gravity 0.963.
Firsts	1			
Seconds	4			
SOYA OIL—				
Crude	2.5	0.25	1	... ...
Fine edible	0.15			
MAIZE OIL—				
Crude	3	0.25	2	... ...
Fine edible	0.15			
COCO-NUT OIL (Technical)—				
Cochin quality	1 lauric	0.25	1	... ...
Ceylon ,,	2 lauric			
Copra	4 lauric			
Fine edible	0.1			

5. We realise that other considerations actually enter into the value of different oils, specially those required for edible purposes. There is at present a very great difficulty in defining systematically such qualities as colour, turbidity, and odour, but it might be possible eventually to secure such a definition.*

6. *Seeds, Nuts, and Kernels, "Good Merchantable Quality."*—We have also considered the definition of "good merchantable quality" in the case of seeds, nuts, and kernels. In this case, too, we have selected the figures from records which different firms have been kind enough to make available, and have sought to establish an average which will tend to the general improvement of the product. In some cases where the same kind of produce is imported from widely differing sources there is necessarily a good deal of variation. Moreover, produce coming from the same source is liable to differ in standard from year to year, and at different periods of the same year.

7. We have nevertheless come to the conclusion that it would be a great advantage to have standards that might be applied with an allowance, over or below, to the seller or to the buyer, for all kinds of produce. We think that such standardisation, even in the case of crops varying so much as cotton seed and linseed from place to place and year to year, would tend to the improvement of the produce, and to better conditions of storage and transport. We have therefore given standards for one or two classes with a view to simplification.

8. The standards which we suggest are calculated on the pure produce, and assume that the determination of shell and dirt has already been carried out. The question whether the oil content of any oleiferous admixture which is not pure produce should be estimated depends on the terms of the contract, and is a commercial matter on which we are not competent to offer a recommendation. As, however, impurities are usually the same kind from the same country of origin, it might be possible to fix an average oil content, if this were required, for the foreign oleaginous admixture.

9. The data in the schedule which we propose conform to those already adopted for the West African Contract, but we have included data for other seeds, nuts, and kernels, which are not covered by that document. The schedule is as follows:—

SCHEDULE OF STANDARDS FOR SEEDS, NUTS, AND KERNELS

	Oil Content.	Percentage of Free Fatty Acids† in Extracted Oil.
Babassu - - - - - - - - -	66	2 (lauric)
Castor-seed - - - - - - - -	47	1
Copra - - - - - - - - -	66	2 (lauric)
Cotton-seed, Egyptian type - - - - -	22	3
,, Indian ,, - - - - -	18	2
Benniseed, gingelly or sesamé - -	54	3
Decorticated ground nuts - - - - -	48	6
Undecorticated ground nuts - - - - -	37	2
Linseed - - - - - - - - -	38	1·5
Mowrah - - - - - - - -	58	...
Palm kernel - - - - - - - -	52	6 (lauric)
Rapeseed - - - - - - - -	43	2
Shea nuts - - - - - - - -	46	10
Soya - - - - - - - - -	17	2

---

* We understand that a Sub-Committee of the Oils and Fats Committee of the Food Investigation Board are now considering the question of palatability of edible oils, and that further research into the general question is in contemplation.

† Calculated as oleic, unless otherwise stated.

10. *Analysis of Feeding Stuffs.*—The method of analysis of oil cake is prescribed under the Fertilisers and Feeding Stuffs Act. As the use of petroleum ether as a solvent has been agreed upon for oleaginous seeds, nuts, and kernels, we should like to suggest that the Board of Agriculture be invited to consider the use of the same solvent for oil cake on the ground that ether at present prescribed as the solvent has a tendency to extract from oleaginous materials non-fatty substances.

11. The schedules referred to us did not include animal fats, but we are willing to investigate these if desired.

We are, Sir,
Your obedient Servants,

(Signed) The Committee of Analysts.

11 Billiter Square, E.C.
5th March 1919.

APPENDIX II

MINISTRY OF FOOD

OILS AND FATS BRANCH

REPORT OF THE COMMITTEE OF ANALYSTS ON STANDARD METHODS OF ANALYSIS OF SEEDS, NUTS, AND KERNELS, FATS AND OILS, AND FATTY RESIDUES.

26th February 1919.

PART I

Determination of Oil in Seeds, Nuts, and Kernels

1. Extract a weighed quantity of the sample prepared for analysis with petroleum ether* in a suitable apparatus for two hours. Remove the partially extracted material, dry, grind in a mortar (grinding may be facilitated by the addition of 1 gm. of fine sand), and again extract until exhausted. If the sample contains a large percentage of oil, it is advisable to grind twice, extracting after each grinding. Evaporate off the solvent, dry at 100° C., and weigh. In the case of oils liable to rapid oxidation, like linseed, drying should be conducted in an inert atmosphere.

2. The extracted oil must be free from solid matter and completely soluble in petroleum ether.

3. In the case of woolly cotton seed, special attention must be paid to obtaining an average sample. The seed must either be crushed by being passed through steel rollers and then thoroughly ground in an iron mortar, or well broken and ground in a mortar.

4. Owing to the variation, both in the amount and composition of the oil in cross sections of the "meat" of copra, it is essential that the portion taken for analysis from the original sample be cut from the pieces at right angles to the rind. The copra must therefore be reduced by shredding or grating at right angles to the rind, or small pieces must be completely shaved down.

5. In the case of castor seed the clean seed with the shell is ground in a mortar which is covered to prevent loss of husk. The extraction must be more prolonged than is the case with other seeds, and is, as a rule, complete in eight hours.

PART II

Fats and Oils

6. In the sample of fat or oil the following constituents are first determined :—

Moisture
Dirt, organic
Ash
Fatty matter (by difference), ——
100

---

* Petroleum ether, volatile without residue at or below 60° C.

7. Upon the clear filtered fatty matter the following determinations are made:—

Acid value.
Saponification value.
Unsaponifiable matter.
Iodine value.

8. The estimations and determinations shall be carried out according to the methods described below.

MOISTURE

9. A "U" tube, one limb of which is an ordinary narrow-bore glass tube and the other a tube about 3 in. long and from 1¼ to 1½ in. in diameter (see Fig. 78, p. 205), is charged in its wider limb with soft blue Cape asbestos, which has been dried at 100° C. The wide limb is provided with a rubber stopper through which passes a narrow tube bent at right angles. The tube, without the stopper, is accurately weighed, suspended by a wire, and about 2 gm. of the well-mixed sample of oil or fat are dropped on to the asbestos, and the whole re-weighed. The stopper is then inserted, and the tube which passes through the stopper is connected with a Kipp apparatus supplying hydrogen, thoroughly dried by passage through strong sulphuric acid.

10. A "U" tube, such as is used in elementary analysis and provided with two glass taps, is filled with glass beads, which are afterwards moistened with strong sulphuric acid. This tube is accurately weighed, after having previously been filled with dry hydrogen, and is then connected with the narrow limb of the asbestos charged tube, the latter being suspended in a beaker containing water kept at a temperature about 10° C. above the melting point of the fat. A slow current of hydrogen is now passed through the whole. When no trace of condensed moisture can be seen in the horizontal limbs of the oil tube and of the weighing tube, which is generally the case after one hour, the latter is weighed, then again attached, and a current of hydrogen allowed to pass for another hour. Minute traces of volatile organic matters, as a rule, produce a slight darkening of the sulphuric acid.

11. The asbestos may advantageously be used in the form of a very porous felt paper produced by pulping the asbestos and running the pulp into a centrifugal which is lined with linen.

12. As an alternative method capable of dealing with a number of samples in one operation, stoppered weighing bottles of about the dimension of the wider limb of the "U" tube used in the standard method may be charged with asbestos, or alternatively, with strips of pleated blotting paper or with paper pulp. These tubes are dried in a vacuum desiccator containing sulphuric acid, and kept at a pressure of 2-5 mm. After weighing, about 2 gm. of the fat or oil are placed in each tube, which is again weighed. The tubes are warmed till the fat is melted, and then replaced into the vacuum desiccator. The air is exhausted, and the desiccator is kept in an incubator at 20° C. for at least forty-eight hours. The weight after that time remains practically constant.

13. The standard method is applicable to all fats and oils, whether readily oxidisable, like linseed oil, or containing high percentages of free fatty acid of low molecular weight, such as lauric.

14. In the case of fats and oils which are free from uncombined fatty acid and not readily oxidisable, the ordinary methods of drying on sand in a water oven may often be used, provided the results are in agreement with those furnished by the standard method.

DIRT AND ASH

15. The percentage of "dirt" in a sample of oil should be arrived at by direct estimation, and not by difference.

16. In the case of a sample containing dirt of such a nature and size as to render it impossible to incorporate the whole of it uniformly throughout the sample, the whole of the sample should be strained through a 25-mesh wire sieve and the solid fragments picked out, weighed, and separately examined.

17. At least 10 gm. of the thoroughly mixed fat or oil is treated with about ten times its volume of hot paraffin oil (kerosene), the insoluble matter filtered off through a weighed filter, washed with hot kerosene, then with petroleum ether. The filter is dried in the water oven to constant weight, incinerated, and the ash weighed.

18. The percentage of ash in the strained oil is determined.

19. The ash in the insoluble matter in the oil is deducted from the ash found in the oil, and this figure is taken as "soluble mineral matter."

ACID VALUE

Definition.

20. The acid value of a fat or oil is a measure of the free fatty acids present, and is defined as the number of milligrams of potassium hydroxide required to neutralise the free fatty acids in 1 gm. of the fat or oil, *i.e.*, parts of potassium hydroxide which are required to neutralise the free fatty acids in 1,000 parts of the fat or oil.

Chemicals Required.

21. (*a*) Alcoholic alkali solution, N/10 and N/2 potassium or sodium hydroxide, accurately standardised.

(*b*) Neutral alcohol, 94-95 per cent. (by volume), containing 0.2 gm. of phenolphthalein per litre. This may be conveniently prepared by redistilling industrial methylated spirits free from mineral oil over sodium hydroxide, adding the phenolphthalein, and subsequently neutralising.

The Test.

22. The necessary quantity of the fat or oil is carefully weighed into a 250 c.c. flask, and about 50 c.c. of the alcohol are added. The mixture is gently boiled, well shaken to thoroughly dissolve out the free fatty acids, and titrated while still warm, and with constant agitation, with N/10 alkali till the pink colour is permanent on shaking for ten seconds. Towards the end of the titration the alkali should be added, drop by drop, in order to avoid excess until the end point is reached.

23. As a rule, 5 gm. of the sample will be found a suitable quantity, but in the case of refined fats or oils this should be increased to 10 gm. If more than 10 c.c. N/10 alkali solution are required for the test, it should be repeated with N/2 alkali.

Then if X = No. of c.c. of N/10 solution,

F = weight of fat or oil taken,

$$\text{Acid value} = \frac{X \times 5.61}{F}.$$

24. In order to express the acidity in percentages of oleic acid, the following formula should be used :—

$$\text{Oleic acid per cent.} = \frac{X \times 2.82}{F}.$$

25. In the case of fats obtained from the kernels of the coco-nut group, such as

coco-nut oil, palm-kernel oil, tucum, babassu, cohune, etc., the acidity is calculated as lauric acid, when the following formula should be used:—

$$\text{Lauric acid per cent.} = \frac{X \times 2.0}{F}.$$

Saponification Value

Definition.

26. The saponification value represents the amount of potassium hydroxide required to neutralise the free and combined acid constituents of a fat or oil, and is expressed in terms of parts of potassium hydroxide per 1,000 parts of the fat or oil.

Solutions Required.

27. (*a*) N/2 hydrochloric acid, accurately standardised.

(*b*) An alcoholic solution of potassium hydroxide or sodium hydroxide, approximately N/2.

Prepared by dissolving 18-20 gm. of stick potassium hydroxide in not more than 10 c.c. of distilled water, and making up to 500 c.c. with 94-95 per cent. (by volume) alcohol, which may be prepared as in par. 21 (*b*). The solution is allowed to stand for twenty-four hours, and the clear liquid siphoned off for use. Potassium hydroxide may be replaced by sodium hydroxide, but this substitution is not desirable. The alcohol must be free from mineral oil, and of such a purity as to yield a nearly colourless solution after twenty-four hours.

(*c*) An alcoholic solution of phenolphthalein, 1 per cent.

The Test.

28. About 2 gm. of the clear filtered fat are accurately weighed into a 200 c.c. flask of resistance glass, 25 c.c. of neutral alcohol added, and 25 c.c. of the alcoholic potassium hydroxide solution accurately measured run in. A like quantity of the same solution is run in, in exactly the same way, into a similar flask, together with 25 c.c. of the neutral alcohol. The flasks are connected to reflux condensers and heated, preferably in a water bath, so that the alcohol boils briskly for thirty minutes. The flask containing the fat should be shaken with a rotary movement from time to time during the period. The contents of the flasks are then titrated while hot, with the N/2 acid, after the addition of 1 c.c. of the phenolphthalein solution.

If:—

F = gm. of fat taken,
X = c.c. of acid required in the control experiment,
Y = c.c. of acid required to neutralise the excess of alkali in the test,

$$\text{then saponification value} = \frac{X - Y \times 0.02805 \times 1000}{F}.$$

$$\textit{N.B.}\text{—The saponification equivalent} = \frac{56100}{S}.$$

Acid Value and Saponification Value

Combination Method

29. The acid value and saponification value may, if so desired, be determined upon the same weight of the sample in the following manner:—

30. About 4 gm. of the clear filtered fat or oil are accurately weighed into the saponification flask, and 25 c.c. of hot alcohol containing 1 c.c. of phenolphthalein solution and previously neutralised, are added. The free fatty acids are titrated from a burette with the alcoholic alkali solution as used for the saponification value,

warming, if necessary, during the titration. The number of c.c. required by the free fatty acids having been noted, such a further quantity of alcoholic alkali as will make a total of 50 c.c. is added, and the process continued, as described above.

31. A blank test is made with 50 c.c. of the alcoholic alkali delivered from the identical burette, using similar quantities of all the reagents. The exact value of the alcoholic alkali having been determined with N/2 hydrochloric acid, the acid value and saponification value may be respectively calculated.

UNSAPONIFIABLE MATTER

32. Unsaponifiable matter in fats and oils includes all substances which are insoluble in water, but soluble in the fat solvents specified below after alkali saponification of the fats and oils.

33. Saponify 5 gm. of the sample with 50 c.c. approximately normal alcoholic KOH, boiling under a reflux condenser for sixty minutes with occasional shaking. Transfer the alcoholic solution to a separating funnel; rinse the flask successively with 50 c.c. of methylated ether, 50 c.c. of petroleum ether, and 50 c.c. of water. Transfer the rinsings to the separating funnel, shaking well after each addition. Allow to separate, and withdraw the soap solution. Repeat the extraction of the soap solution twice, using ether and petroleum ether as before, omitting the treatment with water. The combined ethereal extracts are washed by shaking with slightly alkaline water, allowed to settle, and run through a filter into a tared flask. Wash the filter with petroleum ether, distil off the solvents, dry at 100° C., and weigh the unsaponifiable matter.

IODINE VALUE

34. *Reagents Required:—*

(*a*) *Iodine Solution.*

35. This is conveniently prepared by dissolving 7.5 gm. of iodine trichloride in acetic acid (minimum strength, 95 per cent.), and solution may be hastened by warming on a steam bath. When dissolved, add to the solution 8.2 gm. of resublimed iodine, assist solution by heating as before, and make up to 1,000 c.c. with acetic acid (95 per cent.). The solution is standardised by means of a blank test carried out at the time that it is used, which should be at least twenty-four hours after it is made up. If the solution is heated for a short time by immersion in boiling water, it may be used immediately after cooling.

(*b*) *Sodium Thiosulphate Solution.*

36. Dissolve 24.8 gm. of the pure salt in one litre of distilled water. It is advisable to add 0.5 gm. per litre of sodium bicarbonate to the solution as a preservative. This solution must be standardised by titrating it against pure dry resublimed iodine, but where this is inconvenient, the iodine may be liberated from potassium iodide by a known amount of potassium dichromate in the presence of hydrochloric acid. As the oxidising value of potassium dichromate does not always correspond accurately with that of an equivalent amount of iodine, the potassium dichromate to be used, as described below, shall first be set against pure, dry iodine. The titration is carried out as follows:—

Weigh 0.20 gm. of pure recrystallised $K_2Cr_2O_7$ into a 200 c.c. stoppered bottle, dissolve in 25 c.c. distilled water, add 20 c.c. 10 per cent. potassium iodide solution and 10 c.c. pure HCl, moisten the stopper with the KI solution, and allow to stand five minutes. Wash down the stopper with distilled water, dilute to about 100 c.c. volume, and titrate the liberated iodine with the sodium thiosulphate solution, using starch solution as indicator. A blank test using the potassium iodide solution and hydrochloric acid alone should be carried out, and the necessary deduction, if any, made from the previous titration.

$$0.2 \text{ gm. } K_2Cr_2O_7 = 0.51768 \text{ iodine.}$$

(*c*) *Potassium Iodide Solution.*

37. A 10 per cent. solution of the pure salt in distilled water.

(*d*) *Solvent.*

38. Chloroform or carbon tetrachloride to be used as a solvent for the oil. A blank test on the solvent must not show an absorption of iodine equal to more than 0.2 c.c. of the thiosulphate solution.

(*e*) *Starch Solution.*

39. Use a 1 per cent. solution of soluble starch.

Method

40. 0.15 to 1 gm. of the sample is weighed into a wide-necked stoppered bottle of about 200 c.c. capacity. 0.15 gm. of a strongly drying oil and a proportionately larger amount for oils or fats of lower iodine value, up to approximately 1 gm. for such fats as coco-nut and the like. Dissolve the weighed quantity of fat or oil in 10 c.c. of the solvent (*d*) and add 25 c.c of the iodine solution, moisten the stopper with potassium iodide solution, and allow to stand for one hour. In the case of fats having a very high iodine value like linseed, allow to stand for three hours.

41. After standing, wash the stopper and neck of the bottle down with 15 c.c. of the 10 per cent. potassium iodide solution, mix, and add 100 c.c. of distilled water, and titrate the excess of iodine with the sodium thiosulphate solution. Towards the end of the titration, add about 2 c.c. of the starch solution, and shake vigorously after each addition of the thiosulphate solution until the contents of the bottle are colourless.

42. A blank test using 10 c.c. of fat solvent and 25 c.c. of the iodine solution must be done with each set of estimations, or at least once daily.

43. The result is expressed as per cent. of iodine reacting with the fat.

44. *N.B.*—Where a large number of liquid oils have to be tested, it may be convenient to weigh them by dropping them from a small lipped tube and ascertaining the weight taken by difference, while solid fats can be arranged in small cubes on a suitably sized glass plate and picked up with a pin which has been tared along with the whole; in this case also the weights of the successive pieces are determined by difference until the last piece has been weighed.

SPECIFIC GRAVITY AND VISCOSITY

45. In cases where it is desirable to determine the specific gravity or the viscosity of an oil or fat, the specific gravity shall be determined by the ordinary standard methods, and viscosity by the Redwood Viscometer.

TITRE TEST

46. In cases where it is desirable to determine titer, the method to be adopted is that prescribed by the Seventh International Congress of Applied Chemistry. This method is given in full in J. Lewkowitsch's "Chemical Technology of Oils and Fats," 5th Edition, 1913, Vol. I.

PART III

Fatty Residues

EVALUATION OF SOAP STOCK, ACID OILS AND FATTY ACIDS, COTTON OIL, BLACK GREASE AND MUCILAGE

47. A weighed quantity of the sample (sufficient to give from 1-2 gm. of fatty extract) is introduced into a separating flask (see Fig. 79), 10-20 c.c. of hot water

are added, followed by one drop of methyl orange and a sufficient excess of hydrochloric acid to ensure the decomposition of soap. Five gm. of salt are added, and the mixture is heated gently until the acids separate in a clear layer.

48. The contents of the flask are allowed to cool to about 30° C., and 20 c.c. of petroleum ether, and the liquors are gently agitated, and water is added until the junction of the water and ether rises to the bottom of the centre constriction. When the separation is complete the ether is blown off by means of a siphon and, if necessary, filtered into a weighed flask; 10 c.c. of petroleum ether are introduced into the separating vessel, and again siphoned off. Two further portions of 10 c.c. of petroleum ether are then used, and in these latter cases the flask is closed with a stopper, and gently inverted two or three times after each addition of ether.

49. The mixed ethereal extracts are distilled, and the residue dried at 100° C. and weighed.

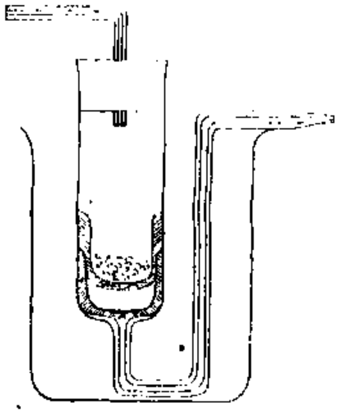

FIG. 78.—Apparatus for Estimating Moisture.

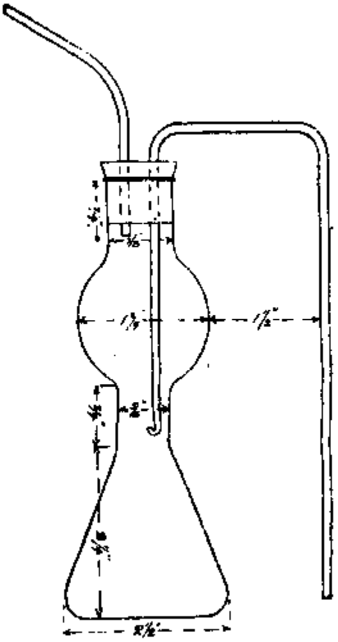

FIG. 79.—Separating Flask for Evaluation of Soap Stock.

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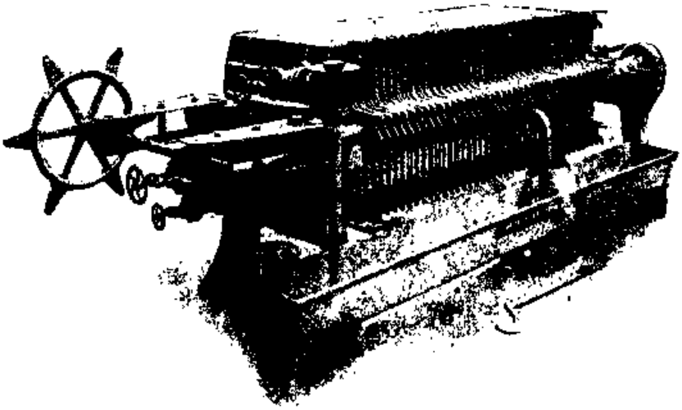

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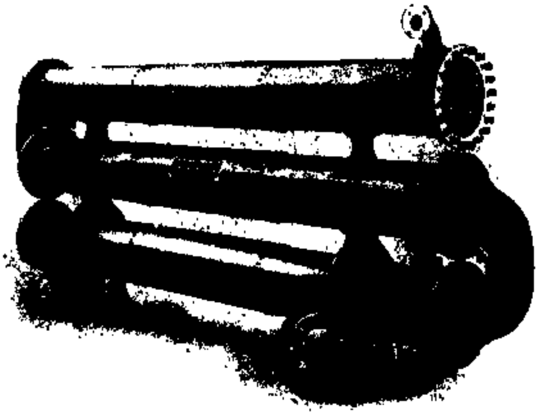

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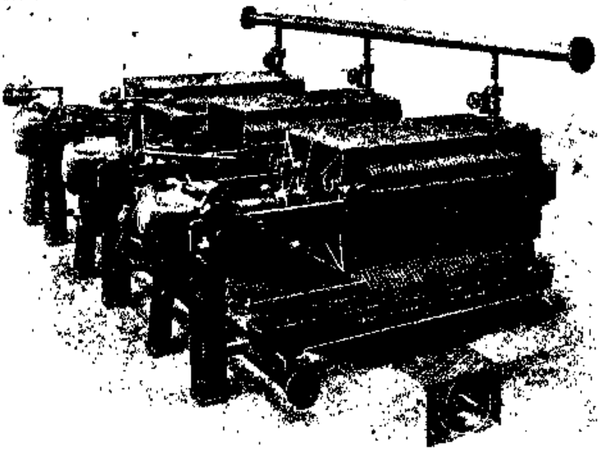

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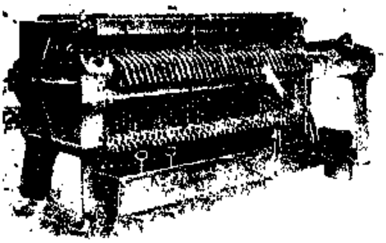

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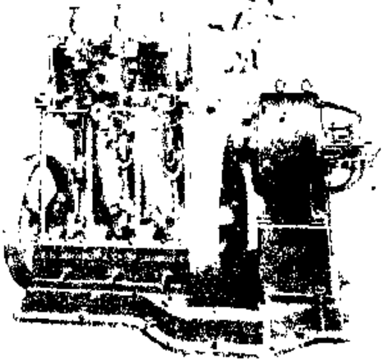

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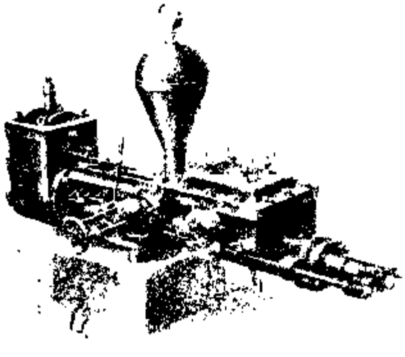

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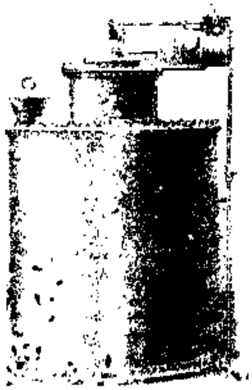

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